

PA 18T91

YATSIMIRSKII, K. B.

USSR/Chemistry - Entropy
Chemistry - Ions

May 1947

"The Standard Entropies of Ions in the Crystalline State," K. B. Yatsimirskii, Chemical-Technological Institute, Ivanovo, 2 pp

"Zhur Fiz Khim" Vol XXI, No 5

Lists the values as discovered by E. N. Gapon and the different values derived by later experimentation.
Published 17 Dec 1946.

18T91

YATSIMIRSKIY, K. B.

JSSR/Chemistry - Ions
Chemistry - Cations

Dec 1947

60710
"Thermochanical Radii of Ions in Solution," K. B.
Yatsimirsky, 4 pp

PA "Dok Akad Nauk SSSR, Nova Ser," Vol LVIII, No 7

Uses method of calculating radii of ions from thermochemical data to calculate this data for several ion species of a lattice from thermochanical and spectroscopic data, according to the equation

$$U = -\Delta H_k - \Delta H_k - \Delta H_{kk}$$

where U is the energy of the lattice,

$$-\Delta H_k, -\Delta H_k$$
60710
USER/Chemistry - Ions (Contd)

Dec 1947

and $-\Delta H_{kk}$ are the heat of formation of a gaseous cation, a gaseous anion, and hard salt. Submitted by Academician I. I. Chernyayev, 18 Jun 1947.

60710

The hexachlorostannate series. L. B. Vankina and N. S. Kurnakov Inst. Gen. Inorg. Chem. Acid. Sci. U.S.S.R., Moscow). *Izv. Akad. Nauk S.S.R.* 1944, *Khim. Nauk* 1948, 263-5; *ibid.* 1946, 461. The heat of the reaction $SnCl_6 + 2M \rightarrow [M_2SnCl_{10}]^{2-}$, in the gaseous state, is taken = 17.3 kcal./mole, and the radius of the $[SnCl_6]^{2-}$ anion = 2.98 Å. (from the K_2SnCl_6 lattice). Then by Pustinskii's equation for the lattice energy (C.A. 38, 5705^a) the heat of formation Ω of the complex salt from the simple salt and the addend = $[2(r_3^2 + 2(n + 1)r_2 + r_1 + 2.98)]/[1 - [0.245/(r_1 + 2.98)] + [287.22/(r_2 + 1)/(r_1 + 1.81)]/[1 - [0.245/(r_1 + 1.81)] - 17.3]$, where r_1 = radius of the cation, 1.81 = radius of $C1^{-}$, r_2 = charge of the cation, n = no. of cations, m = no. of $[SnCl_6]^{2-}$ anions in the mol. Numerical solution of this equation gives the conditions of stability of hexachlorostannates, namely, for salts of the type $M_2[SnCl_6]$, $\Omega > 0$ if $r_1 > 0.4$ Å., for salts of the type $M_2^{\text{III}}[SnCl_6]$, $\Omega > 0$ if $r_1 > 1.8$ Å., and for salts of the type $M_2^{\text{IV}}[SnCl_6]$, $\Omega > 0$ if $r_1 > 3.7$ Å. It accounts satisfactorily for the fact that, although chlorostannates of $[M^{\text{II}}(H_2O)_4]^{2+}$ aquo cations are stable, those of the Cs^{+} simple cations M^{II} are not, as the latter do not attain the crit. size of 1.8 Å. There are no chlorostannates of Ba^{++} or Pb^{++} , as these cations form no stable aquo ions. It further becomes evident why chlorostannates of big cations such as $[M(\text{CO}_3\text{NH}_3)_4]^{2+}$ are stable. The following chlorostannates were prep'd.: By mixing the stoichiometric amts. of FeCl_3 ,

CO(NH₂)₂, and SnCl₄, and evap. on a water bath to be-
geling crystals, one obtains [Fe(CONH₂)₂]·[Cl]·[SnCl₄],
1H₂O, readily sol. in H₂O, stable in air, losing H₂O at
70–80°. with excess SnCl₄, one gets the yellowish [Fe(CONH₂)₂]·[SnCl₄]·1.5H₂O. On mixing concd. solns.
of [Cr(CONH₂)₂]Cl₃ and SnCl₄, one obtains a ppt. of
light-green crystals [Cr(CONH₂)₂]·[Cl]·[SnCl₄], stable
in air, losing H₂O at 90–100°. When the calcd. amts. of
CaCl₂·H₂O and of Cu(NO₃)₂ are dissolved in a 60% aqu.
soln. of SnCl₄, and the soln. is heated 10–20 min. on a water
bath and left in a desiccator over H₂SO₄ for 5–6 days, the
salt [Cu(CONH₂)₂]·[SnCl₄] is pptd. [Mg(CONH₂)₂]
·[SnCl₄] is obtained in an analogous way.

N. Thom

APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2"

YATSIMIRSKIY, K.B.

Yatsemir'skiy, K.B. and Zaslavskiy, I.I. "Classification of diagrams in volumetric analysis of liquid double systems," (reference), Soobshch. o nauch. rabotakh chlenov Vsesoyuz. khim. o-va im. Mendleyeva, 1948, Issue 2, p. 23

SO: U-2888, Letopis Zhurnal'nykh Statey, No. 1, 1949

PL 8/49T13

USSR/Chemistry - Heat of Hydration, Of Ions Jul/Aug 48
 Chemistry - Thermochemistry

"Thermochemical Radii and Heats of Hydration of Ions,"
 K. B. Yatsimirskiy, Inst Gen and Inorg Chem imeni N. S.
 Kurzakov, Acad Sci USSR, 72 pp

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 4

Calculates thermochemical radii and heats of formation
 in the gaseous state of the ions: JO_3^{\cdot} , BrO_3^{\cdot} , CNO^{\cdot} ;

$\text{C}_6\text{H}_5(\text{NO}_2)_3^{\cdot}$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{\cdot}$

Calculates heats of hydration of the ions:

ClO_4^{\cdot} , $\text{C}_6\text{H}_5(\text{NO}_2)_3^{\cdot}$, ClO_4^{\cdot} , BrO_3^{\cdot} , NO_3^{\cdot} , HCO_3^{\cdot} , CNO^{\cdot} ,
 HCOO^{\cdot} , RO_2^{\cdot} , CR_3^{\cdot} , CN^{\cdot} , $[\text{N}(\text{CH}_3)_4]^{\cdot}$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{\cdot}$
 Shows relation between heat of hydration and magnitude

8/49T13

USSR/Chemistry - Heat of Hydration, Of Ions Jul/Aug 48
 (Contd)

of thermochemical radius. This relation for anions of
 the type RO^{\cdot} is somewhat different from that for cations
 anions. Shows applicability of Kapustinskij's
 equation for calculating the entropies of RO^{\cdot} type
 ions in aqueous solution. Presents heat
 of solution of salts as a function of the ion radii
 which form the particular salt. Establishes general
 relationship between alteration of heat of solution and
 the magnitude of the ion radii. Submitted 11 Jun 1947.

8/49T13

YATSMINSKIY, K. B.

PA 27/49T32

USSR/Chemistry - Lanthanum Compounds Sep/Oct 48
Chemistry - Ionization, Potential of

"Calculation of the Potentials of Ionization for Some Lanthanides by Means of Kapustinskiy's Equation," K. B. Yatsmirsakiy, Inst Gen and Inorg Chem imeni N. S. Kurnakov, Acad Sci USSR, Ivanovo Chem Eng Inst, 2 pp

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 5

Found a regular increase in the ionization potential of the lanthanide series, Ce-37.1 ev, Pr-37.7 ev, Nd-38.2 ev, Sm-38.2 ev, and Er-40.0 ev. Submitted 5 Apr 48.

27/49T32

PA 33/49T20

YATSIMIRSKIY, K. B.

USSR/Chemistry - Synthesis

Kor/Dec 48
Chemistry - Energy, Lattice, or Metal Salts

The Lattice Energy of Metal Salts of Secondary Groups in a Periodic System, "K. B. Yatsimirskiy, Inst Gen and Inorg Chem imeni N. S. Kurnakov, Acad Sci USSR, 11 pp

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 6

Studies condensation of 2-formoxybutadiene, 2-methoxybutadiene, and chloroprene with divinylketones (5-methyl-1,4-hexadiene-3-onium and 5-methyl-1,4-octadiene-3-onium). Shows that reaction takes place easily according to general

33/49T20

USSR/Chemistry - Synthesis (Contd)

Kor/Dec 48

diagram of diene synthesis with formation of corresponding pair-substituted derivatives of cyclohexenylketones. Submitted 10 Nov 47.

33/49T20

PA-67/49T40

YATSIMIRSKIY, K. B.

USSR/Chemistry - Salts, Ammine
Cobalt

Dec 48

"Thermochemistry of Cobalt Acidopentammine Salts,"
K. B. Yatsimirskiy, L. L. Pankova, Chair of
Inorg Chem, Ivanovo Chemicotechnol Inst, 7 $\frac{1}{2}$ pp

"Zhur Obschch Khim" Vol XVIII, No 12

Determined heats of formation and heats of
solution for a large number of salts such as
 $(Co(NH_3)_5Cl)Br_2$, $(Co(NH_3)_5SO_4)I$, etc. Made a
study of the thermochemistry of their ions.

67/49T40

2

Extreme points on property curves of binary systems in volume analysis. I. I. Zaslavskii and K. B. Yatsinskii. Zhur. Osnovy Khim. (J. Gen. Chem.) 10, 1755-9 (1949); cf. E.A. 43, 9304. — For ideal binary systems, the d. d. and the at. concn. (total no. of g. atoms in 1 l.) A_m are additive if the compn. is expressed in vol. %; thus, $d_m = d_1 V_1 + d_2 V_2$ and $A_m = A_1 V_1 + A_2 V_2$. In real systems, the deviations Δd and Δd of the real d and d from the ideal A_m and d_m are related by $(\Delta d)/d_m = \Delta d/(A_m)$; $(\Delta d)/d_m = (A_m/d_m)(\Delta d/d V_i)$. It follows from this expression that Δd and Δd can have extreme values at the same point only if $M_1/M_2 = M_2/m_1$, where M = mol. wt., m = no. of atoms in the mol., and, further, that the max. deviation of the component with the smaller "mean at. wt." M/m . By an analogous consideration, the contractions C and dd can have an extreme value at the same point only if the sp. grs. of the 2 components are equal; in the general case, the max. of C is shifted, relative to the max. of dd, in the direction of the component of lower sp. gr. $A_1 = A_2$; in the general case, the max. of dd is shifted, relative to the max. of C, in the direction of the component of higher A . As an illustration, $H_2SO_4 + H_2O$, at 30°, has a max. of dd at 73 wt. % H_2SO_4 ; C at 70%; dd at 60%; $HNO_3 + H_2O$, at 20°, max. dd at 84%; C at 60%; dd at 48-49; dd at 42 wt. % H_2O . In all 3 cases, the max. of dd corresponds to a rational compn.; thus, resp., $H_2SO_4 \cdot 2H_2O$ (between 0 and 100%), $HNO_3 \cdot 3H_2O$ (between 5 and 30%), $H_2O \cdot H_2SO_4$ (between 15 and 40%), whereas the positions of the max. of C and of dd are irrational.

N. Thus

ABE-ELA METALLURGICAL LITERATURE CLASSIFICATION

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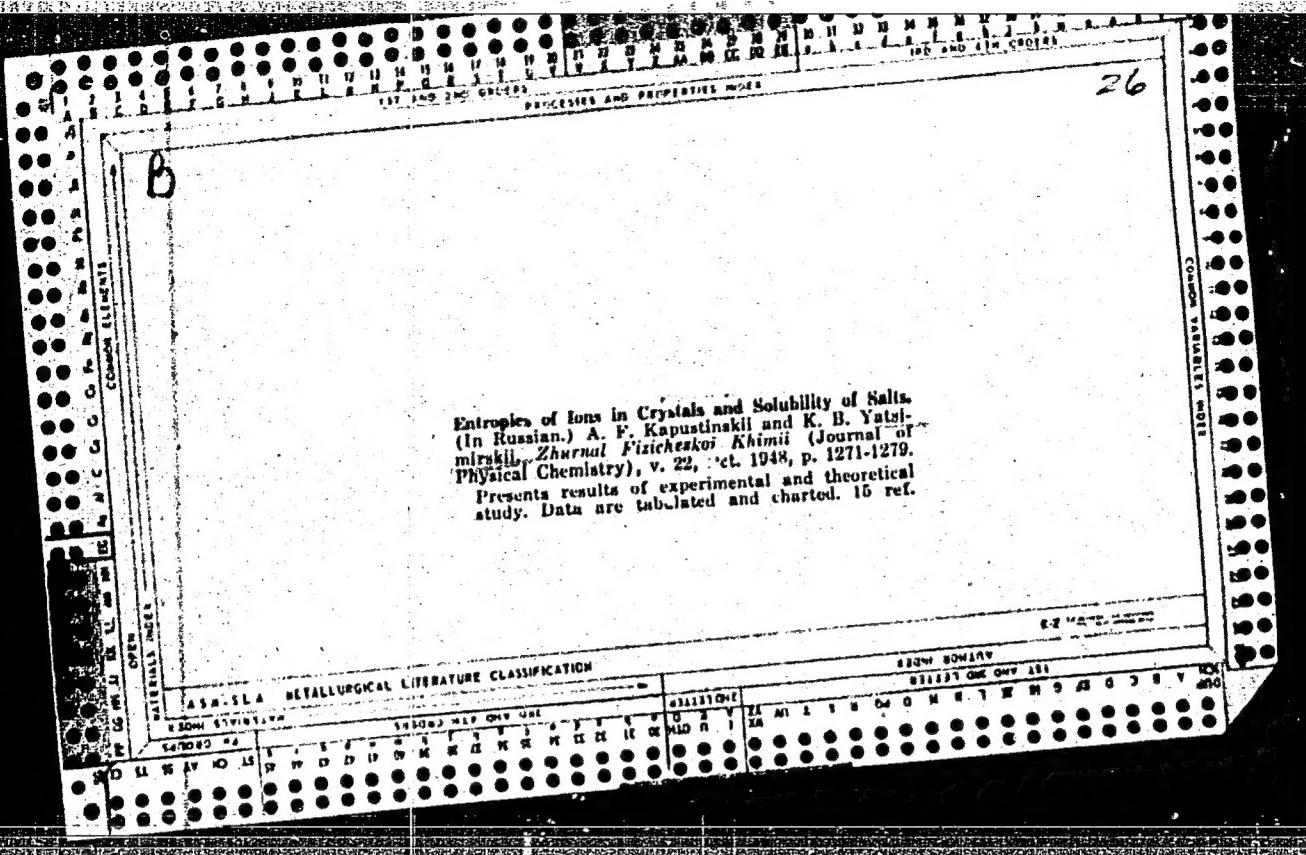
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IATSIMIRSKII, K. B.

I. I. Zaslovskii and K. B. Iatsimirskii, Unusual points on the curves of properties of binary systems during volumetric analysis. p. 1755

Mathematical analysis has established the following for 2-compound systems by chemical reaction: The maximum deviation of atomic concentration from the average of calculated value (ΔA) is shifted in regards to the maximum deviation of specific gravity from the average calculated value (Δd) toward the component with the smaller average atomic weight. The maximum ΔA is shifted in regard to the compression maximum C toward the component with the largest atomic concentration. The maximum Δd is shifted in regards to the maximum C toward the component with the largest specific gravity.

/Chair of Inorganic Chemistry of the Ivanov Chemico Technological Institute
July 17, 1947

SO: Journal of General Chemistry (USSR) 26, (80) No. 10 (1948):

YAKIMIRSKIY, K. B.

K. B. Yakimirskii and L. L. Pankova, Thermo-chemistry of acid-pentaammine salts of cobalt. p. 2051.

The heat of reaction is determined with a 0.26 M solution of Na_2S and from this is calculated the heat of formation of 15 compounds and the heat of solution of 13 compounds. The heat of formation is calculated for a series of complex acid-penta-amino cobalt-ions in a water solution. From this is calculated the heat of formation of certain salts.

Chair of Inorganic Chemistry of the
Ivanov Chemico-Technological
Institute
June 28, 1947

SO: Journal of General Chemistry (USSR) 28, (80) No. 12, (1948)

YATSIMIRSKIY, K.B.

29573

Ie istorii analiticheskoy khimii v rossii. Uspyeekhi Khimii,
1949, vyp.5, s.623-28. Bibliogr: s.628

4. Gyeologo-Gyeograficheskkiye Nauki
(Palyeontologiya - Sm. XV, 5 B)
a. Gyeologo-Gyeograficheskkiye Nauki b Tsyelom. Gyeologiya. Pyetrografiya.
Minyeralogiya. Kristallografiya.

SO: LETOPIS' NO. 40

APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2"

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C.A.

Diagrams of the type ionic radii-property. K. B. Vasil'evskii (Ivanovo Chem.-Technol. Inst., Ivanovo, U.S.S.R.). Izvest. Sektora Fiz.-Khim. Anal., Inst. Obrabotki i Neorg. KМm., Akad. Nauk S.S.R. No. 19, 212-10 (1949). —For this type of diagram where the properties are lattice energy, heat of soln., and soly, cf. C.A. 42, 4602s, 4604s, and 43, 1341s. Analogous diagrams were constructed for ionic radii vs. m.p.s. The diagram ionic radii-crystal structure differed from the preceding ones. When values of r_a were plotted as abscissas and r_b as ordinates, where c and a designate cation and anion, resp., and when line AB was drawn for $r_a/r_b > 0.57$ and line CD for $r_a/r_b = 0.41$, it could be expected, according to Magnus and to Goldschmidt, that to the right of AB the crystal structure would be that of CsCl , yet out of 10 salts 3 crystal, as expected, were of the NaCl type, and 7 had both structures. Similarly, between AB and CD the NaCl type of structure was expected, yet NH_4I having both types of structure was located there. The diagram showed that the CaCl structure appeared where $r_a > 1.6 \text{ \AA}$ and $r_b > 1.9 \text{ \AA}$. Both CaCl and NaCl types occurred where $r_a > 1.35 \text{ \AA}$ and $r_b > 1.7 \text{ \AA}$. Thus, the type of crystal structure depended on the absolute value of r_a . M. Hensch

CA

Thermochromy of complex cobaltic salts with neutral
additives. K. D. Altimarkov and I. L. Paukova (Ivan-
ovo Inst. Chem. Technol.), J. Russ. Chem. U.S.S.R.
19, 509-78 (1948) (English translation). - See C.A. 43,
74034.

CD 2
Thermodynamical relations in the Werner-Miesch series for complex acetato compounds. K. B. Yatsenko, S. I. and L. L. Pavlova (Izdatsovo Inst. Chern. Technol.), J. Russ. Chem. U.S.S.R. 19, 677-88 (1966) (English translation). —See C.A. 65, 7829c.
B. J. C.

The thermodynamical radii and asymptotes of tetrahedral and triangular ions. A. P. Kapustinikh and N. B. Yagodina. (Akad. SSSR, Moscow). Zher. (Mosk.) Khim. (J. Russ. Chem.) 19, 2191-2200 (1949). -(1) Thermodynamical radii r (Å) for a given anion by K. 's equation (*C.A.* 36, 3700) from the lattice energy U show very slight variations, of the order of 3%, depending on the nature of the cation of the salt, in the sense that r of the monovalent anion increases when it is associated with a larger cation;

v_{r} , NO_3^- , varies from 1.80 in CaNO_3 to 1.94 Å. in $[\text{CP}(\text{NH}_3^+)_2\text{Cl}] (\text{NO}_3^-)$; ClO_4^- from 1.98 in RbClO_4 to 2.05 Å. in $[\text{Na}^+] [\text{Ni}^{\text{II}}(\text{ClO}_4)_2]$; HCO_3^- from 1.56 in $[\text{Zn}^+ (\text{NH}_3)_4] (\text{HCO}_3^-)$; SO_4^{2-} from 2.38 in CaSO_4 to 2.33 in $[\text{Co}(\text{NH}_3)_6] \text{SO}_4$; CrO_4^{2-} from 2.37 in $[\text{Co}(\text{NH}_3)_6]\text{Br} / \text{CrO}_4$ to 2.42 in $[\text{Co}(\text{NH}_3)_6] \text{NO}_3 / \text{CrO}_4$; O_4^{2-} , 1.79 in BaO_4 , 1.80 in CaO_4 and SrO_4 . A smaller cation penetrates more deeply into recesses of the anion and thus brings about a decrease of its v_{r} . (2) The heats of hydration Q of anhyd. salts, calcd. by $Q = U_h - U + W$, where U_h = lattice energy of the hydrated salt, the heat of formation W of the gaseous aquo ion from the gaseous central ion and gaseous H_2O remains const. in the case of salts of spherical anions (F^- , Cl^- , Br^- , I^-) but anomalies appear with nonspherical anions; thus, instead of increasing with the size of the anion, Q is greater for chlorides than for nitrates, and the same reversal

is found between bromides and chlorates. This reversal is due to a decrease of the "penetration effect," present in the case of polyat. anions, as a result of the hydration of the cation. Illustrative data of Q_1 in kcal./mole, are: $[Li(H_2O)_4]Cl$ 42.3; $[Li(H_2O)_4]NO_3$ 40.0; $[Mg(H_2O)_6]Cl_2$ 38.9; $[Mg(H_2O)_6](NO_3)_2$ 28.8; $[Mg(H_2O)_6]SO_4$ 26.1; $[Ca(H_2O)_6]Cl_2$ 11.8; $[Ca(H_2O)_6](NO_3)_2$ 10.0; $[Ca(H_2O)_6]SO_4$ 8.4; $[Ba(H_2O)_6](NO_3)_2$ 34.4; $[Ba(H_2O)_6]Br_2$ 16.6; $[Ba(H_2O)_6]ClO_4$ 14.4; $[Ba(H_2O)_6]Cl_2$ 18.3; $[Ba(H_2O)_6]IO_4$ 12.7. (3) The value of r lies somewhere between the min. distance of max. penetration and the radius of the circumscribed sphere. The distance d between the central atom of the complex anion and the cation is not equal to the sum of the thermochem. radii + calcd. for an octahedral surrounding, but, for a given lattice type, the ratio of d and the sum of r is a const.; thus, for the barite type ($BaSO_4$, $BaSO_4$, $PbSO_4$), that ratio = 1.03, and for the calcite type ($CaCO_3$, $MnCO_3$, MnO_2), 0.90. For a given type of anion, the ratio of d and the radius of the circumscribed sphere is a const., thus, for triangular ions (NO_3^- , CO_3^{2-}) it is = 0.67; for tetrahedral ions (ClO_4^- , MnO_4^- , BF_4^- , SO_4^{2-} , CrO_4^{2-} , MoO_4^{2-}) it varies between 0.76 and 0.81, mean 0.79 = 0.03. This relation permits calc.

of r for anions for which the radius of the circumscribed sphere is known; thus, for BO_4^{4-} , r (calcd.) = 1.91, BeF_4^{4-} 2.45, IO_4^{-} 2.49, SeO_4^{2-} 2.43, TeO_4^{-} 2.54, PO_4^{3-} 2.38, AsO_4^{3-} 2.45, SO_4^{2-} 2.60, BiO_4^{4-} 2.68 Å. (4) In groups of the periodic system, the r of anions of analogous structure increase regularly with increasing at. no. of the elements. (5) Heats of formation of the gaseous anion are calcd. by $-\Delta H_A = \Delta H_C - \Delta H_{CA}$ where the subscripts A , C , and CA refer to the gaseous anion, the gaseous cation, and the solid salt, resp., and the ΔH 's are calcd. from the ionization potentials and the heats of sublimation of the metals; for TeO_4^{-} and SbO_4^{4-} , the ΔH_A were calcd. from the heats of formation of the ions in soln. and their heats of hydration Q_h . Values of r , ΔH_A , and Q_h are: NO_3^- 1.89, 80.0, 70.7; ClO_4^- 2.00, 87.8, 64; CHO_4^{2-} 2.36, 91.6, 80; MnO_4^- 2.40, 174, 49; IO_4^- 2.48, 98, (40); CO_4^{3-} 1.85, 47, 317; CrO_4^{2-} 2.4, 182, 229; SO_4^{2-} 2.5, 178, 241; SeO_4^{2-} 2.43, 124, 224; MoO_4^{2-} 2.51, 230, 216; TeO_4^{-} 2.54, 185, (216); WO_4^{2-} 2.57, 266, 203; EO_4^- 1.91, -340, 760; PO_4^{3-} 2.38, 80, 530; AsO_4^{3-} 2.48, -20, 500; BiO_4^{4-} 2.60, -20, (818); NO_3^{2-} 2.4, (-340), -. (6) The calcd. values of $-\Delta H_A$ permit a decision between the Kossel scheme representing the structure of the SO_4^{2-} ion by ionic bonds between a cen-

tral S^{4+} ion and 4 O^{2-} ions, and the Lewis scheme involving covalent bonds between S^{4+} and 4 O^{2-} . The energy of the process $\text{S}^{4+} + 4 \text{O}^{2-} = \text{SO}_4^{2-}$ is calcd. to be 4600 kcal.; that of $\text{S}^{4+} + 4 \text{O}^{2-} = \text{SO}_4^{2-}$ to be 725, as against 7340 and 1000 kcal., resp., from the ΔH_A data. Consequently, the Lewis structure is distinctly predominating. The same holds for the anions ClO_4^- , PO_4^{3-} , SiO_4^{4-} , AsO_4^{3-} , SbO_4^{4-} , NO_3^- , CO_4^{3-} , BO_4^{4-} , ClO_4^{2-} , all of which prove to be predominantly built of singly charged O^{2-} ions covalently bonded with the central ion. The Kossel structures become somewhat more probable as the degree of oxidation of the central ion decreases, but their share never becomes significant. (7) Exptl. determin. of the heat of soln. of NaIO_4 in H_2O at 25° gave -8910 cal.; with the

heat of formation of NaIO_4 in sq. soln. = 96.1 kcal.; this gives for solid NaIO_4 , ΔH_{fus} = -104.0 kcal.

N. Thom...

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Thermochimistry of aqueous salts of manganese. K. D. Valenichuk and A. A. Antshenko (Inzheknizhsvod Klin.-Tikhvin'. Inst.). Doklady Akad. Nauk S.S.R. 69, 381-3 (1946); cf. ibid. 58, 1407 (1947); C.A. 43, 2168d. Owing to the difficulty of prep. $[\text{Mn}(\text{H}_2\text{O})_6]\text{Cl}_2$ with exactly 6 H_2O , the heat of melt. in H_2O , at $25 = 0.05^\circ$, is reported as a mass of 11 cal./mole. Made on prepns. with 4.3, 4.06, 4.08, 3.98, and 3.7 H_2O ; the av. value interpolated to 6 H_2O is 2600 cal., different from the figures of Thomann and of Perrea (C.A. 36, 8820). This gives for the heat of formation $\Delta H_{f,25}^{\circ} = -398.7$ kcal. Further data: of heats of soln. gave: $[\text{Mn}(\text{H}_2\text{O})_6]\text{Br}_2$ 4020 cal.; $\Delta H_{f,25}^{\circ} = -376.1$ kcal.; $[\text{Mn}(\text{H}_2\text{O})_6]\text{I}_2$ 5000 cal.; $\Delta H_{f,25}^{\circ} = -341.0$ kcal.; $[\text{Mn}(\text{H}_2\text{O})_6]\text{Sb}_2$ at 0° (because of the decompr. above 37°) -400 cal.; $\Delta H_{f,25}^{\circ} = -817.8$ kcal. With the previously dtd. heat of addn. of 6 H_2O (gas) to Mn^{++} (gas) -200 kcal., and Mn^{++} (gas) +4 H_2O (gas) = $[\text{Mn}(\text{H}_2\text{O})_6]^{++}$ (gas) -100 kcal., based on the calcs. of May and Evans (C.A. 32, 28877), the heat of formation of the gasous form $[\text{Mn}(\text{H}_2\text{O})_6]^{++}$ is $\Delta H_{f,25}^{\circ} = 177$ kcal. Hence, by the energy difference of the solid salt and the gasous ions, the lattice energy of solid $[\text{Mn}(\text{H}_2\text{O})_6]\text{Cl}_2$ is 480.7 kcal.; and, by the equation of Kramers-Kronig (C.A. 39, 5708), the thermochim. radius of $[\text{Mn}(\text{H}_2\text{O})_6]^{++}$ is 1.61 Å. The calcd. $\Delta H_{f,25}^{\circ}$ values are in very good agreement with the exp. values; but differ, by 11.4-13.7 kcal., from the figures of Bichovskiy and Matanov, which are based on old erroneous data of Leeser (Ann. chim. phys. 28, 425 (1893)). N. Thon

CA 2

Classification of diagrams in volume analysis of liquid binary systems. N. B. Yatsimirskii and I. I. Zaslavskii, (Izv. Akad. Nauk SSSR, Ser. Khim., 1957, No. 10, p. 2211). - Diagrams of the ΔA , const., A as a function of the compn. atc of 4 types: In ideal systems of noninteracting liquids of unchanging degree of assoc., A is a linear function of the compn., and the deviation ΔA from additivity is zero throughout. In systems with one assoc. component which, in soln., dissociates into simpler units, the curve of ΔA is convex to the axis of compn., and ΔA is always neg.. In systems where the components form chem. compds., A is concave to the axis of the compn.. In systems involving both compd. formation and dissociation of one or both assoc. components, the ΔA curve is slightly concave to the axis of abscissas; the abs. values of ΔA are relatively low, and the max. of ΔA may not correspond to the compn. of the compd. Examples of ideal systems are $\text{H}_2\text{-AcOH}$, $\text{C}_2\text{H}_5\text{-CCl}_4$, $\text{C}_2\text{H}_5\text{-PhCl}$, $\text{AcOEt}-\text{HCOEt}$, $\text{C}_2\text{H}_5\text{-PhCl}$, $\text{C}_2\text{H}_5\text{-PhMe}$, $\text{C}_2\text{H}_5\text{-C}_6\text{H}_5\text{Br}$, etc.; for all these systems, plots of ΔA and of the sp. gr. against the compn. in mole fractions are linear, although the viscosity isotherms may show a min. or a max.. Linear plots of ΔA may be found also with systems of assoc. but chemically close substances, as $\text{MeOH}-\text{PrOH}$ and $\text{HCOEt}-\text{AcOH}$. Very slight deviations from additivity, with consistently neg. ΔA , are exhibited by $\text{C}_2\text{H}_5\text{-CS}_2$, PhMe-CS_2 , $\text{CHCl}_3\text{-CS}_2$, $\text{C}_2\text{H}_5\text{-CS}_2$, $\text{C}_2\text{H}_5\text{-CHCl}_3$, $\text{C}_2\text{H}_5\text{-Et}_2\text{O}$, $\text{C}_2\text{H}_5\text{-C}_6\text{H}_5\text{Br}$, etc.; very small pos. ΔA is found in $\text{C}_2\text{H}_5\text{Br-CHCl}_3$ and $\text{CS}_2\text{-PhBr}$. The 2nd type, with dis-

directly neg. ΔA , is exemplified by $\text{C}_2\text{H}_5\text{-AcOH}$, $\text{CCl}_4\text{-Me}_2\text{CO}$, $\text{CS}_2\text{-Me}_2\text{CO}$, $\text{Et}_2\text{Br-AcOH}$, PhMe-AcOH , $\text{CCl}_4\text{-PrOH}$, $\text{Me-Me}_2\text{CO}$, $\text{CS}_2\text{-PrOH}$, etc.; viscosity isotherms of some of these systems may have either a min. or a max., and are, consequently, less informative than the ΔA plots. In the 3rd type, the ΔA curve consists of 2 branches intersecting at the max.; depending on whether, along a branch, A and ΔA are symbiotic, antithetic, or const., the branch is convex to the axis of compn., concave to it, or rectilinear. One single compnd. is indicated by a singular point, whereas in the case of presence of several compds., the max. is rounded, as in $\text{HClO}_4\text{-H}_2\text{O}$, $\text{HNO}_3\text{-H}_2\text{O}$, $\text{HF-H}_2\text{O}$, $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{H}_3\text{PO}_4\text{-H}_2\text{O}$, $\text{NaOH-H}_2\text{O}$, $\text{H}_2\text{SO}_4\text{-Et}_2\text{O}$, etc. "Irrational" systems of the 4th type, showing a flat diffuse max., are illustrated by PhOH-PhNH_2 , $\text{Me}_2\text{CO-HC}_2\text{H}_5\text{I}$, $\text{C}_2\text{H}_5\text{NO}_2\text{-EtOH}$, etc. In the systems $\text{AcOH-H}_2\text{O}$, $\text{MeOH-H}_2\text{O}$, Me_2CO - AcOH , $\text{PhOH-Me}_2\text{CO}$, the max. corresponds to no stoichiometric ratio of the components and to no definite compnd. An S-shaped ΔA curve, resulting from the predominance of the dissociation of an assoc. component along part of the curve, and of compd. formation along another part, is exemplified by the systems $\text{SbCl}_3\text{-C}_6\text{H}_6$, $\text{SbCl}_3\text{-CIPh}_3$, and $\text{SbCl}_3\text{-C}_6\text{H}_5\text{Br}$, where, again, the max. corresponds to no stoichiometric ratio of the components.

N. Thom

CA

2

Classification of complex-forming elements and addends on the basis of energy characteristics. N. B. Vatshlyapkin. (Ivanov Chem.-Technol. Inst.), Zhur. Vsesoyuz. Khim. (J. Gen. Chem.) 20, 1401-7 (1960). In the general case, the energy of formation W of a complex ion from the gaseous central ion and the gaseous addends ("energy of addn.") is composed of electrostatic and covalent terms; specifically, if k is the no. of donor-acceptor covalent bonds in the complex ion, $W = I - nE - nD + U$, where I = total ionization potential, E = electron affinity of the addend, D = energy of the covalent bond between the central ion and the addend, and U = resonance energy of the given structure. On that basis, both complex-forming central elements and addends can be classified, roughly, in 4 groups: (1) "electrostatic," characterized by a high elec. charge, small radius r , high dipole moment, relatively low I , and high E ; examples of central atoms are Al^{3+} , Ti^{4+} , Zr^{4+} , Hf^{4+} , and of addends, F^- , H_2O , ROH , CO_3^{2-} , SO_4^{2-} ; (2) "covalent," characterized by high I , low E , low electrostatic characteristics; examples of central atoms are Au^+ , Hg^{2+} , Pb^{2+} , Bi^{3+} , Ti^+ , addends $\text{S}_2\text{O}_8^{2-}$, I^- , CN^- , Br^- , $\text{CSN}(\text{H})_3$; (3) "universal," characterized by high I , low E , high elec. charge and small r ; examples are Co^{2+} , Pt^{4+} , Rh^{3+} , Li^{+} , Ca^{2+} , Cu^{+} , and the addends ClO_4^- , $\text{Cl}_4\text{O}_6^{2-}$, CN^- ; (4) "intermediate," characterized by medium values of all energy characteristics; examples are Ni^{2+} , Zn^{2+} , Co^{2+} , Fe^{2+} , Ag^+ , Cu^+ , Cd^{2+} , and the addends N_3^- , $\text{Cl}_4\text{N}(\text{H})_3$, NO_2^- , HCO_3^- . Phenomena of group selectivity in complex formation and differences of stability of complex ions in soln. can be interpreted from this point of view.

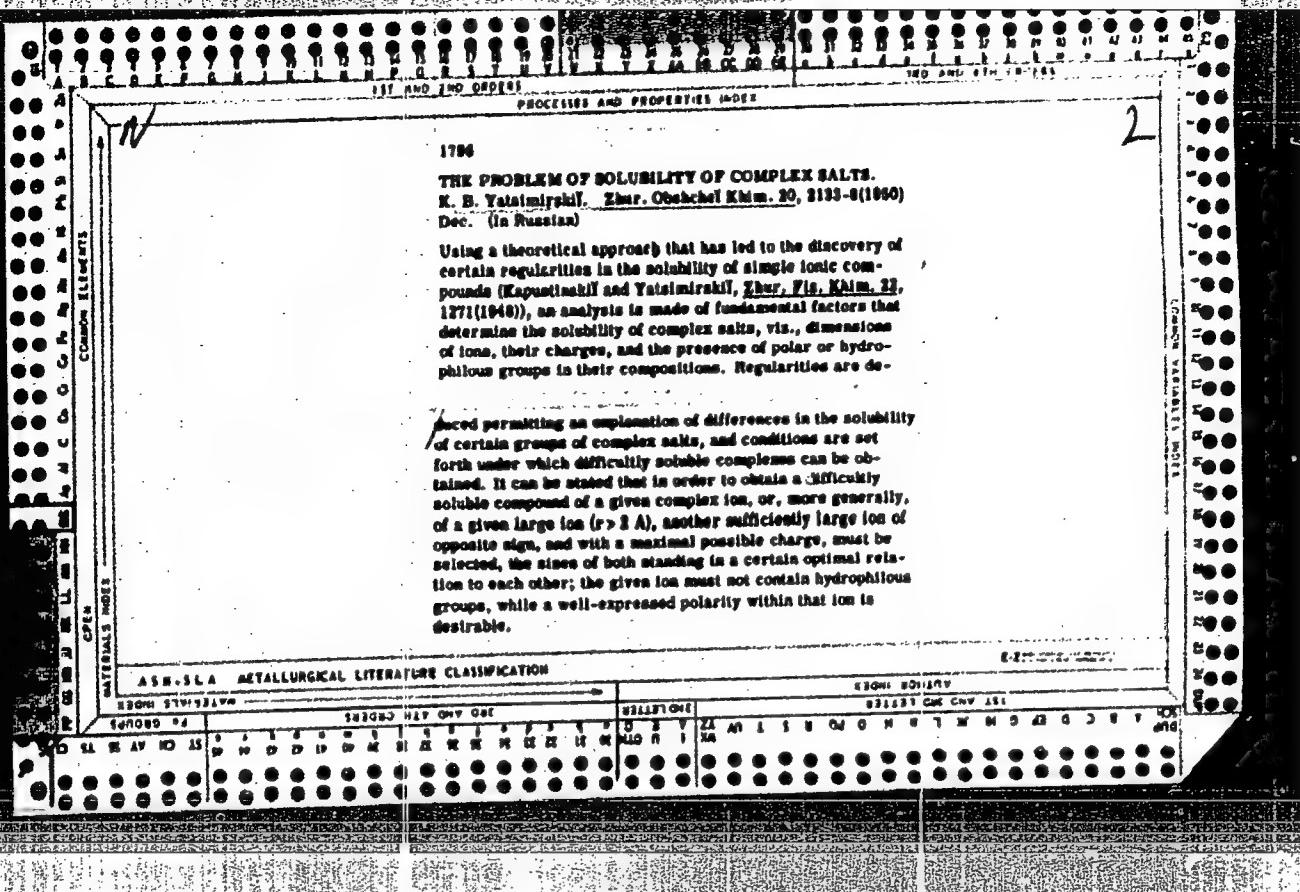
N. Thon

YATSIMIRSKIY, K. B.

CA

Formatopentammine salts of cobalt(III). V. R. II.
Yatsimirskii. Zhur. Obshchey Khim. (J. Gen. Chem.)
20, 1408-11 (1950).—Two new complex salts of Co(III)
were synthesized: $[\text{Co}(\text{NH}_3)_5\text{HCO}_3]_3$ (I), red crystals,
was obtained with a 05% yield by 40-min. heating 5 g.
of Co purplechloride, $[\text{Co}(\text{NH}_3)_5\text{Cl}]_3\text{Cl}_2$, with 100 ml.
of a concn. soln. of HCO_3K contg. approx. an 8-fold
excess of HCO_3K , subsequent mixing of the cooled red
soln. with an equal vol. of satd. KI , and washing the ppt.
with ice water, aq. alc., and finally 80% alc. With a
satd. soln. of NH_4NO_3 instead of KI ; a red ppt. of $[\text{Co}(\text{NH}_3)_5\text{HCO}_3](\text{NO}_3)_2$ (II) was obtained in a 90% yield.
The heats of reaction with a 0.26 M soln. of Na_2S at 25°
were detd., for I, to be -3110 cal./mole, and for II, to be -4560
cal./mole. The heats of soln. in H_2O were detd. to be 14780
and 16300 cal./mole, resp. Hence, and with the use of
the thermochem. data of Bichowsky and Rossini, the
standard heats of formation ΔH_f° of the solid salts were
calcd. to be I -261.2, II -334.3 kcal./mole, and for the
ion $[\text{Co}(\text{NH}_3)_5\text{HCO}_3]^{++}$ in aq. soln. -219.7 kcal./mole.
For the gaseous ion $[\text{Co}(\text{NH}_3)_5\text{HCO}_3]^{++}$, the heat of
formation was calcd. to be 194 kcal./mole with the aid of the
Kapustinskii equation for the lattice energy, with the
thermochem. radius of the ion assumed = 2.30 Å. Hence,
the heat of the reaction $\text{Co}^{+++}(\text{gas}) + 6\text{NH}_3(\text{gas}) +$
 $\text{HCO}_3^-(\text{gas}) \rightarrow [\text{Co}(\text{NH}_3)_5\text{HCO}_3]^{--}(\text{gas}) + \text{IV}$ is $x -$
357 kcal., where x = heat of formation of the gaseous
 Co^{+++} . Consequently, the thermal stability of the gaseous
 $[\text{Co}(\text{NH}_3)_5\text{HCO}_3]^{++}$ is greater than the stability of
all other acidopentammine Co(III) ions, with the exception of $[\text{Co}(\text{NH}_3)_5\text{NO}_3]^{++}$. The stability of these com-
plex ions decreases in the order $\text{NO}_3^- > \text{HCO}_3^- > \text{CNS}^- >$
 $\text{I}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_2^-$.

N. Thom



VATSIMIRSKII, K. B.

Chem

Chem
Thermochemistry of complex compounds with ethylenediamine. K. B. Vatimirskii and A. A. Astashova. Chem.-Tech. Inst. (Vysnovo). Zhur. Osnovnoi Khim. (J. Gen. Chem.) 20, 2130-43 (1957).—Calorimetric measurements at 25° gave for the heats of the reaction of the complex salts with 1 N HCl the following values (en = NH₂CH₂CH₂NH₂): [Cd en]₂Cl₄ 46.43; [Cd en]₂Br₄ 39.2; [Ni en]₂Cl₂2H₂O 30.00; [Ni en]₂I₂ 37.04; [Ni en]₂I₂ 35.41 kcal./mole. From [M en]₂X₄ (cryst.) + 6HCl(aq.) = M⁺⁺(aq.) + 3en H₂⁺⁺(aq.) + 6Cl⁻(aq.) + 2X⁻(aq.) + Q₁, and detns. of the heats of soln., the heats of formation of the complex salts in the standard state were calcd. to: [Cd en]₂Cl₄ 168.8, [Cd en]₂Br₄ 140.0, [Ni en]₂Cl₂ 103.1, [Ni en]₂Br₂ 148.0, [Ni en]₂I₂ 119.6, [Ni en]₂Cl₂2H₂O 309.7, [Ni en]₂Br₂2H₂O 200.4 [Ni en]₂I₂2H₂O 269.0, [Cd en]₂⁺⁺(aq.) 78.3, [Ni en]₂⁺⁺(aq.) 81.5 kcal./mole. The energy, W, of binding of gaseous en by the gaseous metal ion M⁺⁺, to form the gaseous complex ion [M en]₂⁺⁺, is estd. from the lattice energy U of the cryst. complex salts, [M en]₂X₄ (cryst.) = [M en]₂⁺⁺(gaseous) + 2X⁻(gaseous) - U, where U is calcd. by Kapustinskii's equation (C.A. 38, 5705^b), with the thermoelectric radii of all complex ions [M en]₂⁺⁺ = 2.7 Å. This gives for W, Ni⁺⁺ 383, Zn⁺⁺ 372, Co⁺⁺ 372, Fe⁺⁺ 342, Cd⁺⁺ 322 kcal./mole. The order of the heats of binding of 3 en by these ions is the same as that of the heats of binding of 6 NH₃; the latter are lower by 5-13 kcal. From the difference of the heats of formation of the anhyd. and the hydrated salts, the heats of hydration are calcd. to [Ni en]₂Cl₂2H₂O 10.8, [Ni en]₂Br₂2H₂O 5.9, [Ni en]₂I₂2H₂O 3.8. The abnormal increase of the heats of hydration from the iodide to the chloride can be explained by assuming hydration of the anion rather than the cation. N. T.

CA

The solubility of complex salts. N. D. Vatsimirskii
Chem.-Technol. Inst., Ivanovo. J. Gen. Chem. U.S.S.R.
10, 2213-17(1950)(Engl. translation). See C.I., 45,
B. I., M.

2

CA

Energetics of complex compounds. K. N. Yatsimirskii
(Chem. Technol. Inst., Ivanovo). Izv. Akad. Nauk SSSR, Khim.
Nauk. 1951, No. 23, p. 29(10M).—An extensive
discussion of previous work (C.A. 42, 4900c, 1948). M. Ilmeh

1951

CH

Thermochemistry of the trans influence. K. H. Kasten (Ivanov. Chem.-Technol. Inst.), Doklady Akad. Nauk S.S.R., 74, 307-10 (1950). With the heat of formation of the hydrated Co^{+++} ion assumed to be $\Delta H_{f, \infty} = 22$ kcal. from the free energy, with the entropy of the ion in soln. taken equal to that of P^{++} , the following heats of formation of the complex ion in soln. (from the hydrated central ion and addend) are calculated: $[\text{Co}(\text{NH}_3)_6\text{Cl}]^{++}$ (I) +0; $[\text{Co}(\text{NH}_3)_5\text{NO}_3]^{++}$ (II) 33.1; $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{++}$ (III) 41.7; $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{++}$ (IV) 45.0; 1.6-[$\text{Co}(\text{NH}_3)_5\text{NO}_3$] (V) 53.1; 1.2-[$\text{Co}(\text{NH}_3)_5\text{NO}_3$] (VI) 51.0; 1.6-[$\text{Co}(\text{NH}_3)_5\text{Cl}_2$] (VII) 32.0; 1.2-[$\text{Co}(\text{NH}_3)_5\text{Cl}]^+$ (VIII) +0.2; 1.6-[$\text{Co}(\text{NH}_3)_5\text{NO}_3$] (IX) 49.3; 1.6-[$\text{Co}(\text{NH}_3)_5\text{NO}_3\text{H}_2\text{O}$] (X) 47.0; $[\text{Co}(\text{NH}_3)_5\text{NO}_3\text{Cl}]^{++}$ (XI) -0.6; $[\text{Co}(\text{NH}_3)_5\text{NO}_3\text{Cl}_2]$ (XII) -1.3; $\text{X} \rightarrow \text{IV}$, -0.6; $\text{IX} \rightarrow \text{III}$, -7.6; $\text{XII} \rightarrow \text{VI}$, -1.3; $\text{X} \rightarrow \text{V}$, -11.4; $\text{IX} \rightarrow \text{VII}$, -17.3 kcal. Heats of displacement of NH_3 by Cl^- : $\text{V} \rightarrow \text{II}$, -0.8; $\text{II} \rightarrow \text{I}$, -1.3; $\text{X} \rightarrow \text{IV}$, -0.6; $\text{IX} \rightarrow \text{III}$, -7.6; $\text{XII} \rightarrow \text{VI}$, -1.3; $\text{X} \rightarrow \text{V}$, -11.4; $\text{IX} \rightarrow \text{VII}$, -17.3 kcal. Heats of displacement of NH_3 by H_2O : $\text{V} \rightarrow \text{X}$, -7.8; $\text{II} \rightarrow \text{IV}$, -8.1; $\text{II} \rightarrow \text{III}$, -3.8; $\text{X} \rightarrow \text{IV}$, -3.8; $\text{IX} \rightarrow \text{VII}$, -17.3 kcal. Heats of displacement of NH_3 by NO_3^- : $\text{II} \rightarrow \text{IX}$, -3.8; $\text{I} \rightarrow \text{III}$, -10.2; $\text{III} \rightarrow \text{VII}$, -9.7; $\text{III} \rightarrow \text{VIII}$, -11.5. Displacement of NH_3 by H_2O : $\text{II} \rightarrow \text{X}$, -7.6; $\text{I} \rightarrow \text{IV}$, -6.9; $\text{II} \rightarrow \text{III}$, -3.3 kcal. These figures illustrate the possibility of thermochemical measurement of the trans influence. In the case of Co^{+++} complexes, the series is $\text{NO}_3^- > \text{NH}_3 > \text{H}_2\text{O} > \text{Cl}^-$. The susceptibility to trans influence decreases in that order, i.e. the heat effect accompanying the

displacement of NO_3^- is greatest when the trans position is occupied by NH_3 or H_2O , somewhat smaller if it is occupied by Cl^- in the trans position. In the displacement of 2 NO_3^- , the thermal effect is greatest with XII, smaller with XI, and neg. with NH_3 in trans position to NO_3^- . The same rules apply to displacement of NH_3 and H_2O by Cl^- ; the heat is greater with NO_3^- in trans position to NH_3 or H_2O than with NH_3 or Cl^- in that position. This order is reversed in the displacement of Cl^- by any of the addends considered. These facts can be interpreted by assuming that, of the two d-, one s-, and three p-bonds of the octahedron, the d-bonds are the most addend-stable, and that the different addends have unequal tendency to occupy a d-bond. This tendency appears to decrease in the order $\text{NO}_3^- > \text{NH}_3 > \text{H}_2\text{O} > \text{Cl}^-$. For NO_3^- , the bond strength differs greatly, depending on whether the NO_3^- group is bound by σ - or by δ -bonds; this difference is less pronounced for NH_3 and H_2O , and seems to disappear completely for Cl^- . This conclusion is borne out by the heats of formation ΔH_f of geometric isomers. Croco-ions, with one NO_3^- group bound by a σ -bond, the other by a δ -bond, have a lower ΔH_f than flavo-ions, with both NO_3^- groups δ -bonded. In the case of praseo- and violo-salts, the trans isomer, with the Cl^- ion bound by σ - and δ -bonds, has the higher ΔH_f , probably as a result of the ionogenic nature of the N. Then

YATSIMIRSKIY, R. S.

Thermochemistry of complex compounds Moskva, Izd-vo Akademii nauk
SSSR, 1951. (Mic 53-843 Collation of the original: 250 p.

Microfilm T-14

183T24

USSR/Chemistry - Analytical Reactions Jul/Aug 51
and Reagents

"Classification of Analytical Reactions and Reagents on the Basis of the Energy Characteristics of Ions," K. B. Yatsimirskiy, Ivanovo Chem-Technol Inst

"Zhur Analit Khim" Vol VI, No 4, pp 211-217

"Covalent characteristic" of given ion, or tendency of ion to form covalent bond (calcd as difference between ion's ionization potential and its heat of hydration), electron charge, and ionic radius provide data for classification of ions for analytical

183T24

USSR/Chemistry - Analytical Reactions Jul/Aug 51
and Reagents (Contd)

"Gives tables of above values for many purposes. Gives rules for prediction of solv when anions and cations are present in soln.

183T24

YATSIMIRSKIY, K. B.

LC

Complex compounds with anions of aromatic sulfonic acids in the outer sphere. K. P. Yatsimirskij, K. E. Polikarpov, L. V. Svirskaya, and V. V. Starostin (Chem.-Technol. Inst., Ivinovsk), Zhur. Obshch. Khim. (J. Gen. Chem.) 21, 480-90 (1951). Mixing 1% solns. of aromatic sulfonates (Na salts) with dil. aq. solns. of $[Cr(NH_3)_6]Cl_3$ (I), $[Cr(NH_3)_6](NO_3)_3$ (II), or $[Cr(C_6H_5NH_3)_6]Cl_3$ (III) usually gave ppts. of the corresponding complex salts. $p\text{-Me}_2\text{Ph}-\text{H}_2\text{SO}_4\text{Na}$ gave with I and III ppts. having compns. of the type $[Cr(NH_3)_6](C_6H_5NH_3\text{SO}_4)_2$. The soln. of the Cr salt is 0.0037 mole/l. at 20°. Na sulfate does not give ppts. $C_6\text{H}_5\text{CH}_2\text{SO}_4\text{Na}$ gives ppts. with I, II, and III; $[Cr(NH_3)_6](C_6\text{H}_5\text{CH}_2\text{SO}_4)_2$, green; $(C_6\text{H}_5\text{CH}_2\text{SO}_4)_2$, yellow; $[Cr(CO_2\text{H})_6](C_6\text{H}_5\text{CH}_2\text{SO}_4)_2$, green. The 2-nitro analog gives ppts. with I, II, and III; $[Cr(NH_3)_6](C_6\text{H}_5\text{NO}_2\text{SO}_4)_2$, yellow; $[Cr(NH_3)_6](C_6\text{H}_5\text{NO}_2\text{SO}_4)_2$, green, 0.0087 mole/l. at 40°; $[Cr(CO_2\text{H})_6](C_6\text{H}_5\text{NO}_2\text{SO}_4)_2$, green also, 0.0033 mole/l. at 20°. The 2-Chloro-5-nitro analog also gives ppts. with I, II, and III; $[Cr(NH_3)_6](C_6\text{H}_5\text{ClNO}_2)_2$, green; yellow; $[Cr(CO_2\text{H})_6](C_6\text{H}_5\text{ClNO}_2)_2$, green. Na 3-carbazolesulfonate gives ppts. even in rather dil. solns. with I, II, and III. Even less sol. are the salts of 6-nitro-3-carbazolesulfonic acid; $[Cr(NH_3)_6](C_6\text{H}_5\text{N}_3\text{SO}_4)_2$, yellow; $[Cr(CO_2\text{H})_6](C_6\text{H}_5\text{N}_3\text{SO}_4)_2$, yellow; poorly sol. salts also form with derivs. of Cu, Zn, Ni, and Cd. Especially poorly sol. are salts of alizarinsulfonates; salts with I and II are especially mentioned but are not further characterized.

Generally, the solv. declines with increased size of the anion and with introduction of polar groups into it. Introduction of OH, NH₂, or COOH groups into the sulfonate radical sharply raises the solv. of the complex salts. Sepn. of some sulfonic acids by such means may be feasible. G. M. K.

10

Unsaturated cyclic hydrocarbons and their halogen derivatives. XI. Transformation of

184T33

YATSIMIRSKIY, K. B.

USSR/Chemistry - Analytical

Feb 51

"Problem of the Variation of Free Energy and Entropy in Reactions of Formation of Complexes," K. B. Yatsimirskiy, Chair of Analyt Chem, Chemicotech Inst, Ivanovo

"Zhur Fiz Khim" Vol XXV, No 2, pp 221-223

Advances hypothesis, based on entropy data for R_0^{2-} ions (i.e., CC_2^{2-} , MoO_4^{2-}), that only thermochem radius determines entropy of single-type complex ions (i.e., those having equal number of same groups combined to cen ion). Shows difference between heat effect and free energy to be const in single-type

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Feb 51

complex formation. Arranges anions and cations by decreasing stability, latter assumed to be detd by difference between ionization potential of cen atom and heat of hydration of ion formed.

184T33

(A)

Stability constants of some complex compounds of lead.
N. B. Yal'nikov (Chem.-Tech. Inst., Ivanovo), Zhur. Pb. Khim. 25, 478-9 (1951).—Barber theoretical predictions (C.I. 49, 6110f) concerning the relative stability of complexes in soln. are verified by expts. leading to the defn. at 25° of the stability consts. $K_1 = [Pb(SO_4)_2]^{-1}/[Pb^{2+}]^2[S_2O_3^{2-}]^2$, $K_2 = [Pb(SO_4)_2]^{-1}/[Pb^{2+}]^2[S_2O_3^{2-}]^4$ and $K = [Pb(CNS)_2]^{-1}/[Pb^{2+}]^2[CNS^{-}]^4$. The values $K_1 = 1.35 \times 10^5$ and $K_2 = 2.23 \times 10^4$ are obtained by measuring the solv. of PbS_2O_3 in aq. solns. of Na_2SO_4 . The solv. product of PbS_2O_3 is also calc'd.: 3.99×10^{-1} . The value $K = 0.5$ is found by measuring the solv. of $Pb(CNS)_2$ in aq. solns. of $KCNS$. The solv. product of $Pb(CNS)_2$ is 2.00×10^{-4} . Finally, the stability const. $K' PbBr_2^-$ is estd. from the data of Burrage (C.I. 20, 3412); it is approx. 2×10^4 . These values of K_1 , K_2 , K and K' confirm the theory. Michel Boudart

"APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2

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6

CN

Complex compounds with anions as coordination centers.
 K. H. Yuzimuraki (Izumoya Chem.-Technol. Inst.). *Dokl. Akad. Nauk S.S.R.* 77, 819-22(1951).—Pavlov's conditions for the formation of complex ions with cations as addends to an anion as central atoms are low electron affinity of the anion and high electron affinity of the cation, i.e., low and high ionization potentials, resp., of the corresponding atoms. In aq. soln., the ionic magnitude is the difference of electron affinity and energy of hydration; consequently, favored addends will be cations with both high electron affinity and large radius, particularly Au^+ , Ag^+ , Hg^{2+} , Cd^{2+} , and Pb^{2+} . The double salts found in the systems $\text{AgCl}-\text{AgNO}_3$, $\text{AgBr}-\text{AgNO}_3$, and $\text{AgI}-\text{AgNO}_3$, should thus be formulated $[\text{AgI}] \text{NO}_3$, $[\text{AgI}] (\text{NO}_3)_2$, $[\text{AgBr}] \text{NO}_3$, and $[\text{AgCl}] \text{NO}_3$. From data of Hellwege (Z. anorg. Chem. 25, 167(1900)) on the solv. of Ag halide in solns. of AgNO_3 , the following equil. consts. are estd.: $[\text{Ag}^{+}] [\text{I}^-] / [\text{AgI}]^2 = 2 \times 10^{-6}$; $[\text{Ag}^{+}] [\text{Br}^-] / [\text{AgBr}]^2 = 0.8 \times 10^{-6}$; $[\text{Ag}^{+}] [\text{Cl}^-] / [\text{AgCl}]^2 = 2 \times 10^{-3}$. Thus, the stability of these complexes increases with decreasing ionization po-

tential of the anion element, i.e., from chloride to iodide. In the search for analogous complexes with addend cations other than Ag^+ , determinations were made of the solv. of HgI_2 in aq. solns. of $\text{Hg}(\text{NO}_3)_2$; selected data are, for $\text{Hg}(\text{NO}_3)_2$: 0.1789, 0.7210, 1.2123, 1.4534, 1.8587 moles/1000 g. H_2O ; HgI_2 : 14.5, 65.8, 110.3, 148.0, 209.3 millimoles/1000 g. H_2O . The fast increase of the solv. indicates presence not only of HgI^+ but also of HgI_2^{2-} . From the solv. data, the equil. consts. are $[\text{Hg}^{+}]^{111} / [\text{HgI}_2^{2-}] = 4.1 \times 10^{-6}$; $[\text{Hg}^{+}]^{111} / [\text{HgI}_2^{2-}] = 2.1 \times 10^{-6}$. Further complexes of this type, which should be formulated $[\text{HgSiX}_3]$, $[\text{CdSiX}_3]$, $[\text{HgSeBr}_3]$, $(\text{ClO}_4)_2$, $[\text{PbSiX}_3]$, $[\text{AgS}] \text{NO}_3$, $[\text{AgSe}] \text{Cl}_2$, $[\text{HgSe}] \text{Br}_2$, there are also more highly complex ions, such as $[\text{HgSiX}_3]$. Examples of complexes with a 5th-group element as central atom are the compds. described by Pötsch and Thümmel (Ber. 16, 2435(1883)), $[\text{AgPb}](\text{NO}_3)_2$, $[\text{AgAs}](\text{NO}_3)_2$, and $[\text{AgSb}](\text{NO}_3)_2$.

1951

CP

The periodic law of D. I. Mendeleev and the stability of complex compounds. A. A. Grinberg and K. B. Yatsimishvili. Izdat. Akad. Nauk S.S.R., Odz. Khim. Nauk, 1952, 211-17.—The tendency to complex formation is characterized quantitatively by the energies of formation of the gaseous complex ions, and by the initalability const. K of the complex; the latter magnitude actually expresses the difference of the stability of the complex ion and of the corresponding aquo ion. From a thermocycle, cycle involving the formation of a complex ion $[MA_n]^{+*}$ from $M^{+*} + nA$, the heat is $\Delta H = (W_1 - W_2) + (I_1 - I_2) + n(\lambda_1 - \lambda_2)$, where W_1 and W_2 are the energies of adiab. of H_2O and of A , resp., I_1 the gaseous M^{+*} , I_2 and I_3 are the heats of hydration of $[MA_n]^{+*}$ and $[M(H_2O)]^{+*}$, resp., and λ_1 and λ_2 the heat of evapn. of H_2O and of hydration of A , resp. The latter term being const. for reactions of one type, and the middle term approx. const., $\Delta H = (W_1 - W_2) + C$ (const.), and $RT \ln K \approx (W_1 - W_2) + C$ (const.). This gives the relation between the 2 characteristics of the tendency to complex formation. This relation is verified by data for $[Ag(NH_3)]^{+*}$, $[Co(NH_3)]^{+*}$, $[Ni(NH_3)]^{+*}$, $[Co en]^{+*}$, $[Ni en]^{+*}$, and $[Zn en]^{+*}$. In application to ions with an inert-gas structure of the outer electron shell, but different charge and radius, this leads to the conclusion

that the stability of complexes increases from left to right in the period and decreases from top to bottom in the groups of the periodic system. For ions with 18-electron shells, the complex stability ought to decrease with increasing at. no. in the group if the bond is predominantly ionic; with predominantly covalent bonding, elements of the fifth period should form particularly stable complexes. As a result of the 2 antagonistic factors, the heat of formation of gaseous complex ions within a subgroup may pass through a minimum: examples are, for complex ions $[M(NH_3)_6]^{+*}$, $M = Cu$ 131, Ag 101, Au 101 kcal./mole, and for ions $[M(NH_3)_6]^{+*}$, $M = Zn$ 200, Cd 311, Hg 370 kcal./mole. The same is found for the free-energy change $\Delta F = RT \ln K$ of formation of complex ions in aq. soln. The more pronounced is the covalent character of the bond, the more marked is the increase of the stability (ΔF) of the complex ions from top to bottom; this is illustrated by comparison of ΔF for complex chlorides, bromides, and iodides, the latter showing the most marked change of ΔF from Cu to Au or from Zn to Hg, and the chlorides the least marked. In series of complex ions formed by central ions with the same charge, but with different outer-electron shell structures, the complex sta-

YATSIMIRSKIY, K.B.; ASTASHEVA, A.A.

Slightly soluble complex compounds of thiourea and their use in analysis.
J. Anal. Chem. U.S.S.R. 7, 45-9 '52 [Engl. translation].
(CA 47 no.19:9849 '53)

YATSIMIRSKY, K.B.

Chemical Abst.
Vol. 48 No. 8
Apr. 25, 1954
Analytical Chemistry

Thermodynamic criteria for the applicability of chemical
reactions to volumetric analysis. E. B. Yatsimirskii
(Ivanovo Chem. Techn. Inst.). J. Russ. Phys. Chem. Soc.,
7, 239-242 (1922) (Engl. translation). See Col. 47, 1-196.

YATSIMIRSKIY, K. B., SHUTOV, A. A.

Mercury Compounds

Instability constants of complex mercury-iodide compounds. Zhur. fiz. khim. 16 no. 6, 1952

Monthly List of Russian Accessions. Library of Congress. November, 1952, Unclassified.

YATSIMIRSKIV, K.B.

Chemical Abst.
Vol. 48 No. 9
May 10, 1954
Inorganic Chemistry

Some ternary complexes of copper and silver. ³ K. B. Yatsimirskii and V. E. Purova (Voronezh Inst. Chem. Technol.). *J. Gen. Chem. U.S.S.R.* 22, 1324-33 (1952) (Engl. translation); *Zhur. Oshchel Khim.* 22, 1284-9 (1952).—When halides of Cu (I) and Ag dissolve in solns. of $S_2O_3^{2-}$, mixed complexes of the type $[MeX_2S_2O_3]^{m-n}$ are formed. The solubilities of CuI and $CuCNS$ in thiosulfate solns. were measured at various temps., and the stability consts. were calcd. for the resultant $[Cu(S_2O_3)_2]^{m-n}$ and $[Cu(CNS)S_2O_3]^{m-n}$ as 3.1×10^{-11} and 1.3×10^{-10} , resp. On the basis of literature data for the solubilities of Ag halides in thiocyanate and thiosulfate solns., the following stability consts. were calcd.: $[Ag(CNS)]^{m-n}$, $1.0 \pm 0.5 \times 10^{-11}$; $[AgICNS]^{m-n}$, 7.1×10^{-11} ; $[AgClS_2O_3]^{m-n}$, 0.7×10^{-10} ; $[AgBrS_2O_3]^{m-n}$, 4.1×10^{-11} ; $[AgIS_2O_3]^{m-n}$, 2.7×10^{-12} .

Bernard Rubin

9-3-54
JF

YATSUMIRSKIY, K.B.

Chemical Abst.
Vol. 48 No. 9
May 10, 1954
General and Physical Chemistry

(2) Chem

The absolute contraction constant and the periodic law
I. I. Zagorkin and K. B. Yatsumirskii. *J. Gen. Chem.*
(U.S.S.R.) 22, 1763-6 (1952) (Engl. translation).—See C.A.
47, 1098e. H. L. M.

9-3-37
gyp

YATSIMIRSKIY, K. B.

Chemical Abst.
Vol. 48 No. 9
May 10, 1954
General and Physical Chemistry

② C.I.C.
Thermochemistry of nickel-ammonia complexes in
aqueous solution. V. K. B. Yatsimirskii and V. M. Grafova.
J. Gen. Chem. (U.S.S.R.) 22, 1765-9 (1952) (Engl. transla-
tion).—See *C.A.* 47, 2030e. H. L. H.

YATSIMIRSKIY, K. B.

Compounds, Complex

"Thermochemistry of complex compounds."
Reviewed by O. Ye. Zvyagintsev. Zhur. prikl.
khim., 25, No. 7, 1952.

Monthly List of Russian Accessions, Library of Congress, November 1952, UNCLASSIFIED.

YATSIMIRSKIY, K. B.

USSR /Chemistry - Cadmium and Lead
Compounds

Feb 52

"Entropy Changes During Formation of Complex Halides
in Aqueous Solutions," K. B. Yatsimirskiy, A. A.
Astasheva, Ivanovo Chem-Technol Inst

"Zhur Fiz Khim" Vol XVI, No 2, pp 239-243

Calcd. entropy changes occurring during formation of
some halide and cyanide complexes as well as std
entropies for 11 complex ions and mols in sq soln
(2 tables). Detad heats of mixing of $\text{Ca}(\text{NO}_3)_2$ and
 $\text{Pb}(\text{NO}_3)_2$ solns with KI solns. On the basis of exptl
data, calcd heat effects of formation of ions

211T49

CaI_4^- , PbI_4^- , CaI_3^- in sq soln as well as contin-
gent entropy changes. Showed that published re-
sults on heats of formation of CaCl_2 and PbI_4^- are
in need of correction.

211T49

*Inorganic chemistry**CIA*

Constants of instability of mercury-lodine complex compounds. [C. Yu. Yatsulinskii and A. A. Sbitov (Chem. Technol. Inst., Ivanovo). Zhar. Fiz. Khim. 26, 842-7 (1952).] The solv. S of HgI_2 in 0.026 M, 0.090 M, 0.268 M, 0.503 M, 0.844 M, 1.058 M, 1.345 M, and 1.681 M $\text{Hg}(\text{NO}_3)_2$ at 25° is 10, 25, 275, 443, 684, 928, 1290, and 1538×10^{-4} mole/l. Except the last two, these values can be represented by $S = 0.0224 c^{1/2} + 0.0895 c^{1/2}$, in which c is the concn. of Hg^{2+} , complete dissociation being assumed. The increase of S with c cannot be explained by the ionic strength J of the solv. as S increases with c also when J remains const. (in solns. of $\text{Mg}(\text{NO}_3)_2$ and $\text{Hg}(\text{NO}_3)_2$ at $J = 0$). As S contains terms in $c^{1/2}$ and $c^{1/2}$, the increase of S is due to formation of $[\text{Hg}]^{1/2}$ and $[\text{Hg}]^{1/2}$ ions. From the above equation $A_1 K_1 = 0.0224$ and $A_1 K_2 = 0.0895$; A_1 is the solv. product of $[\text{Hg}]^{1/2}$, $K_1 = 7.06 \times 10^{-10}$ is the instability const. of $[\text{Hg}]^{1/2}$, and $K_2 = 1.77 \times 10^{-10}$ is the instability const. of $[\text{Hg}]^{1/2}$. The solv. was detd. in the usual manner and also by titrating $\text{Hg}(\text{NO}_3)_2$ solns. with KI to opalescence.

J. J. Bikerman

YATSKHINSKY, K.P.

Investigation of bismuth halide complexes by the solution method. X $\times 10^{-4}$ for $[BiCl^{+4}]/[H^4]$ and for the corresponding bromide method. K D Vaynshteyn (Chem. Eng. Inst., Moscow) The curve $\log S \propto \log [HNO_3]$ for $BiONO_3$ is a straight line at low HNO_3 concen., and in this range the

X = 1 and Br in various concns. of $HClO_4$ and HNO_3 the fraction for all concns. proceeds by 1. The graph of $X = 1$ and Br in various concns. of $HClO_4$ and HNO_3 shows for variable KX concns. are curved lines. A general HNO_3 with variable concns. of $HClO_4$ and HNO_3 leads to different values of K (e.g., 10, 45, 45, 45, 45) and those of both series of assumptions and limitations leads to different values of K (e.g., 10, 45, 45, 45, 45). The equations that provide a graphic method for the value of K are given below.

For the first series of assumptions and limitations, the equation is: $X = 1 + \frac{K}{1 + K} \cdot \frac{1}{1 + \frac{1}{X}} \cdot \frac{1}{1 + \frac{1}{X}}$.
For the second series of assumptions and limitations, the equation is: $X = 1 + \frac{K}{1 + K} \cdot \frac{1}{1 + \frac{1}{X}} \cdot \frac{1}{1 + \frac{1}{X}}$.

YATSIMIRSKIY, K.B.

4

The calculation of the dissociation constants of stepwise complex formation from polarographic data. K. B. Yatsimirskii (Chem.-Technol. Inst., Ivanovo). *Soviet Sci.-Tech. Uchebniye Kursiki Akad. Nauk S.S.R.*, 1, 193-9 (1953).

The standard equations used for the calcn. of equil. const. from polarographic data are derived on the assumption of a single equil. reaction, $MX^{p+} \rightleftharpoons M^{n+} + pX^-$. When stepwise complex formation occurs, it is necessary to add another equil.: $MX_1^{p+} \rightleftharpoons MX_2^{p+} + X^-$ (for notations cf. Stromberg, et al., *C.A.* 43, 5691e). This leads to relations that, upon differentiation and limitation to the case where the concn. of both complex ions is the same, become $d\Delta E/d \log C_s = A(p + 0.5)$ and $\Delta E = A(\log C_r^{p+} - \log K_{p+1} + \log 2)$, where $A = 0.059/\pi$. The tangent for $p = 1, 2$, etc., is drawn to the ΔE vs. $\log c$ curve, and thus p , ΔE , and $\log C_s$ are obtained. Dissoci. consts. of known complexes calc'd. by this method agree with, or are of the same order of magnitude as, those calc'd. by the older, simplified method.

I. Bencowitz

smj jek

YATSIMIRSKIY, R.B.

Stability of different degrees of oxidation of the elements.

K. B. Yatsimirskii [Chem. Technical Inst. (university)]
USSR Ministry of Chemical Fertilizers, Moscow, USSR
2000 X 1000 - The oxidation of the main elements of the periodic system
and their compounds. Moscow, 1941. 210 p.

Statement by Ag. 11 and 12. The results of the research of the stability of the different degrees of oxidation of the elements of the periodic system and their compounds. It is suggested that 44 elements and 44 isotopes are proposed by the data of Syrikovskii et al. 44 isotopes in which the respective authors highlighted higher degrees of oxidation of an element in the system. The author of the article is K. B. Yatsimirskii.

YATSIMIRSKII, K. B.

Chem 4
②

Chemical Abst.
Vol. 48 No. 4
Feb. 25, 1954
Analytical Chemistry

The nature of the so-called "weighting effect." K. B.
Yatsimirskii (Ivanov Chem.-Technol. Inst.), Zhur. Anal.
Khim., 8, 314-20(1953).—The "weighting effect" first proposed by Feigl (C.A. 19, 1108) according to which an increase in the mol. wt. of a reagent increases the sensitivity of the latter toward a given reaction is not strictly true. The analysis outlined in C.A. 43, 1241 and 45, 3089 is applied here to org. reagents. It is shown that addn. of various groups into an analytical reagent causes a change in the free energy of its lattice. Replacement of H in a C-H group by some other group causes a change in the log of solv. ($\Delta \log S$) by approx. the same value. For OH, $\Delta \log S \sim 1.5$, i.e. the solv. increases approx. 30 times. For other groups $\Delta \log S$ is for Cl⁻ -0.60, CH₃ -2.1, Cl⁻ -0.4, Br⁻ -0.5, and I⁻ -1.0. The effect of added CH₃ groups was studied on Li, Ca, and Ba fatty acid salts. For these salts $-\Delta \log S/n$ was calcd. where n is the no. of CH₃ groups. Each addnl. CH₃ caused the log S to decrease by an av. of 0.28. Addn. of aromatic rings caused a greater decrease in the solv. of the ppt. but at the same time reduces the solv. of the reagent which leads to a reduction of its sensitivity. M. Jlosch

YATSIMIRSKIY, K.B.

Stability of complex compounds in aqueous solutions. Uspokhi Khim. 22,
410-44 '53. (MIRA 6:4)
(CA 47 no.19:9841 '53)

YATSIMIRSKIY, K.B.

USER:

Electrode and ionization potentials

K. B. Yatsimirskiy

In case of some ions the method was more effective. The following results for some cases are given. No. 1 - Pb^{++} of $\text{In}^{+1.38}$ was measured. No. 2 - Cu^{++} of $\text{Cu}^{+1.38}$. No. 3 - Ag^{++} of $\text{Ag}^{+1.36}$. In all cases the values of the radius were in agreement with those given by other authors. No. 4 - Na^{+} to Ca^{++} , Mg^{++} , Al^{++} , Si^{++} , Cr^{++} , Mn^{++} , V^{++} , and mG^{++} , and the results were in satisfactory agreement with exp. values. Requirements in the change of ionic radius with at. no. were described.

J. J. Casey

YATSIMIRSKIY, K.B.; GRAKOVA, Z.M.

Thermochemistry of cuprammonium complexes in water solution. Zhur,ob.
khim. 23 no.5:717-720 My '53. (MLRA 6:5)

1. Ivanovskiy khimiko-tehnologicheskiy institut.
(Thermochemistry) (Compounds, Complex)

YATSIMIRSKIY, K.B.

Chemical Abst.
Vol. 48 No. 6
Mar. 25, 1954
Inorganic Chemistry

Nickel-Dimethylglyoxime complexes. K. B. Yatsimirskiy
and Z. M. Goralova. *Zhur. Obshchey Khim.* 23, 938-41
(1953).—The reaction between NiSO_4 and dimethylgly-
oxime in ammoniacal soln. In the presence of atm. O_2 ,
yielded a colored (I) and a colorless (II) complex compd.
The ratio of Ni:dimethylglyoxime in I was 1:3; in II, 1:1.
The calcd. equil. const. checked well with the exptl., ob-
tained by measuring the optical density of I at different
concn's. A. P. Kotloby.

MF
11-5-54

YATSIMIRSKIY, K. B.

Instability constants of iodide-cadmium and iodide-lead complexes. K. B. Yatsimirskii and A. A. Shitov (Chem.-Technol. Inst., Ivanovo). *Zhur. Fiz. Khim.* 27, 782-91 (1953); cf. *C.A.* 46, 11602d. — The calcd. instability constns. of the complex ions $(\text{CdI})^{+++}$, $(\text{CdI})^+$, $(\text{PbI})^{+++}$, and $(\text{PbI})^+$ at 25° were 8.16×10^{-4} , 8.41×10^{-4} , 3.18×10^{-1} and 5.05×10^{-1} , resp., by measurement of the solv. (S) of PbI_3 in aq. solns. of $\text{Pb}(\text{NO}_3)_4$ and $\text{Cd}(\text{NO}_3)_2$ of various concns. S depended on the cation concns. according to the empirical equations $S_1 = 0.037[\text{Cd}]^{1/2} + 0.0236[\text{Cd}]^{1/4}$ and $S_2 = 0.0032[\text{Pb}]^{1/2} + 0.00075[\text{Pb}]^{1/4}$. The calcd. relative activity coeffts. (γ) of PbI_3 in aq. solns. of Ca , Mg , and Zn nitrates are tabulated for concns. of the latter from 0.2 to 2.4M; values of γ for 1M solns. are 0.225, 0.309, and 0.319, resp., where γ for PbI_3 in satd. aq. soln. is arbitrarily equal to unity. The solv. product of PbI_3 calcd. from exptl. data by the method of Kapustinskii (*C.A.* 38, 2870), is 1.05×10^{-4} .

I. W. Jawshew, Jr.

YATSIMIRSKY, K. B.
*Thermodynamics of anhydronates. K. B. Yatsimirskii
and V. V. Kostikov (Chem. Technol. Inst., Ivanovo).
Zhur. Akad. Nauk SSSR, Ser. Khim., 1953, v. 33, p. 6384.*
The heat of reaction (H) of a 24.3% HCl min. (II) with crystalline
An⁻ An⁻ (I), An⁻ An⁻ (III), An⁻ IV, NaAn, V, LiAn,
VI, TlAn⁻, VII, and VIII, where An⁻ = Cl⁻, Br⁻, I⁻, SCN⁻, F⁻, ClO⁻, SO²⁻, PO³⁻, and ClO⁻ in 1M HCl are measured at 25°. The
pH of the solution was measured at 25°. The heat of reaction is calculated by the equation:
$$\Delta H = A \cdot \log_{10} \frac{K_1}{K_2}$$
 where $A = -25.1 \text{ kcal/mole} \cdot \text{deg}^{-1}$. The
calculated lattice energies of II to VIII have the
value $K_1 + A_1$, where $A_1 = 44.1, 122, 164$, for I,
682.3, and 627.1 kcal./mole, resp., and K_2 is the heat of
formation of the An anion. J. W. Lowenberg, Jr.

YATSIMIRSKIY, K. B.

USSR /Chemistry - Cadmium, Palladium, Oct 53
and Bismuth Compounds.

"Thermochimistry of Complex Thiourea Compounds
in Aqueous-Solutions," K. B. Tatsimirskiy, A. A.
Astasheva, Ivanovo Chem-Techmol Inst

Zhur Fiz Khim, Vol 27, No 10, pp 1539-44.

Dstd the heat of mixing of solns of the salts
 AgNO_3 , $\text{Hg}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, CdI_2 , $\text{Pd}(\text{NO}_3)_2$,
 $\text{Bi}(\text{NO}_3)_3$, and CuCNS with thiourea solns of dif-
ferent concns. Dstd the changes of enthalpy

272112

and entropy in connection with the formation of
complex ions from Ag^+ , Cu^+ , Cd^{2+} , and Pb^{2+} with
thiourea. Estimated the constant of instability K of
 $[\text{Hg}(\text{thiourea})_4]^{2-}$ to be 1.1×10^{-33} on the basis
of thermochemical data.

272112

YATSIMIRSKIY, K.B.

USSR.

Use of dimethylphenylbenzylammonium as reagent for large anions. K. B. Yatsimirskiy and V. I. Blagoveshchenskaya. Trudy Komissii Anal. Khim., Akad. Nauk S.S.R., Otdel. Khim. Nauk 5(8) 90-3 (1954); cf. Emde, C.A. 53, 2470.—The $\text{Me}_2\text{Ph}(\text{PhCl}_2)\text{N}^+$ ion was added to solns. of different anions. I pptd. CrO_4^{2-} , SO_4^{2-} , $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{4-}$, and iodide. Sensitivity of these reactions was detd. The crystals were photographed. A 1M soln. of ICI was mixed with 0.5M solns. of salts of the anions. With SO_4^{2-} white dendrites pptd. from concd. solns. (above 0.5%). Dil. solns. gave crystals. A 1M ICI soln. did not form a ppt. in solns. contg. <0.1% SO_4^{2-} but when a ICI crystal was added to 1 drop of such dil. SO_4^{2-} soln. crystals of LiSO_4 formed rapidly. Min. concn. was 1:2000, detectable min. 0.5 γ. Solv. of LiSO_4 increased greatly by heating. The salt was recrystd. from hot H_2O , dried over H_2SO_4 , and analyzed for S and N. With $[\text{Fe}(\text{CN})_6]^{4-}$ yellow crystals, $\text{Li}_2\text{Fe}(\text{CN})_6 \cdot \text{H}_2\text{O}$, formed. Min. concn. was 1:2000, detectable min. 0.6 γ. Compon. was confirmed by N and $[\text{Fe}(\text{CN})_6]^{4-}$ testas. With $\text{Cr}_2\text{O}_7^{2-}$ yellow crystals with an unusual form pptd. from very dil. soln. Min. concn. was 1:2000, detectable min. 0.88 γ. Analysis for $\text{Cr}_2\text{O}_7^{2-}$ confirmed the formula $\text{Li}_2\text{Cr}_2\text{O}_7$. With $[\text{Fe}(\text{CN})_6]^{4-}$, ICI gave a ppt. only in the presence of acid. These fine greenish cubes are much less sol. in H_2O than the tetracyanide salt. Min. concn. was 1:17,000, detectable min. 0.059 γ. Detn. of N and $[\text{Fe}(\text{CN})_6]^{4-}$ confirmed the formula $\text{LiH}_2\text{Fe}(\text{CN})_6 \cdot \text{H}_2\text{O}$. From iodide solns. a crystal of ICI pptd. I iodide as confirmed by analysis. Min. concn. was 1:400, detectable min. 2.5 γ. Burilla Mayerle

USSR/Chemistry

Card 1/1 : Pub. 145 - 5/10

Author:

APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2"

Title :

Energy characteristics and analytical classification of ions

Periodical :

Zhur. anal. khim. 9/5, 282-292, Sep-Oct 1954

Abstract :

The basic energy characteristics of ions, which determine mainly their behavior in a solution and the electro-affinity of the ion in an aqueous solution, are explained. Judging by the magnitude of electro-affinity all cations can be divided into three groups; ions with low electro-affinity forming water-soluble sulfides; ions with mean electro-affinity values forming sulfides soluble in acids but not in water, and ions with high electro-affinity forming non-soluble sulfides. All three groups belong to mono-, di- and tri-charge ions with an electro-affinity of 30, 70 and 190 kcal. Five USSR references (1950-1952). Tables.

Institution :

Submitted : November 26, 1953

Yatsimirskiy, K. B.

USSR/Chemistry

Card 1/1 Pub. 151 - 10/36

Authors : Yatsimirskiy, K. B., and Yasinskene, E. I.

Title : The kinetics of aquation of Cr urea complexes

Periodical : Zhur. ob. khim. 24/1, 55-61, Jan 1954

Abstract : The constants of the rate of reaction leading to the aquation of hexaurea-chromion in an aqueous solution were measured at 30, 40, 50 and 60° temperatures. The activation energy was computed. The rate of reaction of hexaurea-chromion activation was also investigated by an optical method and the results are listed. Seven references: 4-USA; 2-USSR and 1-German (1903-1952). Tables; graphs.

Institution : The Chemical-Technological Institute, Ivanovo

Submitted : September 14, 1953

YATSIMIRSKILYK. B.

USSR/Chemistry

Card 1/1 Pub. 151 - 5/42

Authors : Yatsimirsikly, K. B.

Title : Factors determining the stability of certain complex compound groups
in aqueous solutions

Periodical : Zhur. ob. khim. 24/9, 1498-1507, Sep 1954

Abstract : The effect of increased central ion charge on the stability of complexes
in aqueous solutions, especially in the case of addenda-anions with
small radii or high charges, is explained. The stability of complexes
with large addenda increases with the increase in radius of the central
ion; the stability of complexes with small addenda and amino-acids de-
creases with increase in radius of the complex forming cation. The
polarizing effect of isochoric ions was characterized by means of in-
stability constants. Fifteen references: 4-USSR; 11-USA (1948-1953).
Tables; graphs.

Institution : Chemical Technological Institute, Ivanov

Submitted : March 25, 1954

YATSIMIRSKIY, K.B.

USSR/ Chemistry - Physical chemistry

Card 1/1 Pub. 147 - 6/26

Authors : Yatsimirskiy , K. B., and Shutov, A. A.

Title : On the thermochemistry of certain iodide complexes

Periodical : Zhur. fiz. khim. 28/1, 30-35, Jan 1954

Abstract : The change in the heat content and entropy which occurs during the formation of complex ions $[HgJ]^+$, $[CdJ]^+$ and $[PbJ]^+$ was established from the experimental data regarding the heats of blending KI solutions with $Hg(NO_3)_2$, $Cd(NO_3)_2$ and $Pb(NO_3)_2$ solutions. The specific heats of these solutions were established. The heats of formation of the iodide complexes were estimated on the basis of the heats of decomposition of solid complex $[Ag_3J](NO_3)_2$ and $[HgJ]NO_3$ salts with water and Na_2S solutions. Six references 5-USSR and 1-French (1876-1953). Tables.

Institution : The Chemical Technological Institute, Ivanovo

Submitted : February 16, 1953

YATSIMIRSKIY, K.B.

GRINBERG, A.A. (Leningrad); BABAYEVA, A.V. (Moscow); YATSIMIRSKIY, K.B.
(Ivanovo); GOREMYKIN, V.I. (Moscow); BOLIY, G.B. (Moscow); TIAL-
KOV, Ya.A. (Kiev); YAKSHIN, M.M. (Moscow); KEDROV, B.M. (Moscow);
GEL'MAN, A.D. (Moscow); FEDOROV, I.A. (Moscow); MAKSIMYUK, Ye.A.
(Leningrad); VOL'KENSHTEYN, M.V. (Leningrad); ZHDANOV, G.S. (Moscow);
PTITSYN, B.V. (Leningrad); ABLOV, A.V. (Kishinev); VOLSHTEYN, L.M.
(Dnepropetrovsk); TROITSKAYA, A.D. (Kazan'); KLOCHKO, M.A. (Moscow);
BABAYEVA, A.V.; TRONEV, V.G. (Moscow); RUBINSHTEYN, A.M. (Moscow)
CHERNYAYEV, I.I.; GRINBERG, A.A.; TANANAYEV, I.V.

Explanation of the transeffect. Izv. Sekt. plat. i blag. met. no.28:
56-126 '54.
(Compounds, Complex) (Platinum)

(MLRA 7:9)

YATSIMIRSKIY, K. B.

USSR/ Chemistry Physical chemistry

Card : -1/1 Pub. 147 - 17/25

Authors : Yatsimirekiy, K. B., and Zolotarev, E. K.

Title : On the thermodynamics of oxalate complexes

Periodical : Zhur. fiz. khim. 28/7, 1292 - 1298, July 1954

Abstract : Experimental data on the thermodynamics of oxalate complexes. The heat of blending solutions of homologous salts, with potassium and ammonium oxalate solutions, was determined for the purpose of estimating the enthalpy changes of such complexes. The instability constants of complex ions: Mn, Co, Ni, Cu, Zn $(C_2O_4)_2^{2-}$ and Fe $(C_2O_4)_3^{3-}$, were determined. Nineteen references: 8 USA; 7 USSR; 1 Italian and 3 German (1903 - 1952). Tables; graph.

Institution : Chemical-Technological Institute, Ivanov

Submitted : November 16, 1953

"APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2

APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2"

YATSIMIRSKIY, K. B.

✓ Quantitative characteristics which determine the suitability of complex compounds for volumetric analysis
Ch. B. Yatsimirskiy (Inst. Chem. Technol., Ivanovo)

Zhur. Anal. Khim. 10, 61-8(1955); J. Anal. Chem. U.S.S.R. 10, 85-9(1955)(Engl. translation).—In titration of complex-forming metals and in titration with such metals the max. degree of accuracy is determined by the dissociation const. of the complex formed and by the initial concns. of the reactants. The accuracy of a titration is considered to be determined by the ratio of the concn. of the given substance at the equivalence point to its initial concn. (*C.A. 47, 1620b*). The inverse logarithm of this ratio, designated by μ_f , is referred to as the index of titration accuracy. For a reaction of the type $M + A = MA$ a relation $\text{const. } \mu_f = \text{const. } \log(\text{dissoc. const. of } MA)$ is derived, under the assumptions that the initial concns. of M and A are equal and that the changes in vol. upon titration are negligible. Where dissociation occurs in more than 1 step, the equation is somewhat more complex. The min. pH at which a titration with a certain degree of required accuracy can be carried out can be calculated. Fitting or masking accompanying elements into complexes is essential in certain cases of titration. The completeness of masking is determined by the ratio of the equiv. concns. of the masking and masking reactions and by the concns. of the reactants. A set of equations is derived which express the completeness of masking. In certain procedures of volumetric analysis the sought-for ion is first converted into a complex ion and then ppt'd. The applicability of this method depends primarily on the sol. product of the complex salt formed. Conditions for suitability of colored end-point indicators are derived.

M. Illoch

"APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2

APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2"

"APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2

Use of complements in analytical chemistry

APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2"

"APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2

YATSIMIRSKIY, K.B.

*/Application of complexes in analytical chemistry. II
Lab 21. 1976-83 (1985)*

APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2"

YATSIMIRSKIY, K.B.

VASIL'YEV, V.P.; YATSIMIRSKIY, K.B.

On E.A.Ukshe and A.I.Levin's article "Composition and properties
of a complex electrolyte in a copper-pyrophosphate bath." Zhur.
ob.khim.25 no.6:1233-1235 Je '55. (MIRA 8:12)

1. Ivanovskiy khimiko-tehnologicheskiy institut.
(Electrolytes) (Ukshe, E.A.) (Levin, A.I.)

YATSIMIRSKIY, K.V. (Ivanovo)

Thermodynamics of complex compounds of elements from the middle
of the fourth period of Mendeleev's system. Uch.zap.Kaz.un. 115
no.10:50-51 '55. (MLRA 10:5)
(Compounds, Complex)

"APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2

YATSIMIRSKIY, K.B.

APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2"

YATSIMIRSKIV, K.B.
USSR/Physical Chemistry - Atom

B-3

Abs Jour: Ref Zhur-Khimiya, No 5, 1957, 14336

Author : Yatsimirskiy K. B.

Inst :
Title : Special characteristics of thirteen-electron ions

Orig Pub: Zh. neorgan. khimii, 1956, 1, No. 1, 96-99

Abstract: An examination is made of the relationship between the characteristics of bi-and trivalent ions of elements of the fourth period from Sc to Ga and the structure of the electron shells. It is shown that, in the series Ti^{2+} , V^{2+} , Cr^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , and Sc^{3+} , Ti^{3+} , V^{3+} , Cr^{3+} , Mn^{3+} , Fe^{3+} , Co^{3+} , Ni^{3+} , Cu^{3+} , Ga^{3+d5} (thirteen p-electron), the ions Mn^{2+} , Fe^{3+} disturb the monotonous nature of the variation of certain characteristics: ionization potentials, oxidation potentials, ionic radii, heats of hydration, strength of compounds formed by these ions, vapor pressures of halide dissociation, crystalline structure of sulfides and

Card 1/2 Chemical Technol. Inst., Ivanovo.

USSR/Physical Chemistry - Atom

B-3

Abs Jour: Ref Zhur-Khimiya, No 5, 1957, 14336

Abstract: selenides of the type MX, rates of formation and decomposition of complex compounds. Disturbances of the monotony take place also in the case of Zn^{2+} and Ga^{3+} . All the disturbances are explained by the order in which the d-nuclei are filled by the electrons.

Card 2/2

YATSIMIRSKIY K.B.

USSR/Inorganic Chemistry - Complex Compounds, C

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 678

Author: Yatsimirskiy, K. B.

Institution: None

Title: Concerning Certain Functions Characteristic of Stepwise Complex Formation in Solutions

Original Periodical: Zh. neorgan. khimii, 1956, Vol 1, No 3, 412-421

Abstract: The basic functions which characterize stepwise complex formation in solutions are discussed: the "formation function" \bar{n} , the "degree of complex binding" ϕ (giving the ratio of the total concentration of the metal to the concentration of free metal ions), the "fraction of the given complex" α_m (giving the ratio of the concentration of a given complex (MA_m) to the sum of the concentration of all complexes and the free metal ions). The relationships between \bar{n} , ϕ , and α_m have been established, and the method for calculating any one of these functions from the others is indicated; \bar{n} , ϕ , and α_m can be calculated from the

Card 1/2

USSR/Inorganic Chemistry - Complex Compounds, C

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 678

Abstract: experimental data obtained during the study of stepwise complex formation by the solubility method, the distribution coefficient, ion exchange, by the potentiometric method, by the polarographic method, etc. Formulas are given relating the functions under discussion to experimentally measured values. From a series of values of \bar{n} , ϕ , and α_m it is possible to calculate the equilibrium constant for each step. Current methods for calculating the equilibrium constants are discussed and an improvement of a method previously proposed by the author is presented (Referat Zhur - Khimiya, 1954, 41064, 46234).

Card 2/2

"APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2

YATSIMIRSKIY, K.B.

/The kinetics and mechanism of the formation of wet 1

APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2"

USSR/Inorganic Chemistry. Complex Compounds.
YATSIMIRSKIY, K. B.

Abs Jour : Referat. Zhurnal Khimiya, No 6, 1957, 18847

Author : K. B. Yatsimirskiy, I. I. Alekseyeva.

Inst : Study of Oxalate and Phosphate Complexes of Molybdenum by the Kinetic Method

Orig Pub : Zh. Neorgan. Khimii, 1956, 1, No 5, 952-957

Abstract : The equilibrium in solutions of oxalate and phosphate complexes of Mo was studied on the basis of the measurement of the speed of the reaction of iodide oxidation by hydrogen peroxide in an acid medium. This reaction is catalyzed by molybdic acid (I) (RZhKhim, 1956, 78:55). A decrease of the concentration of I in consequence of the formation of complexes causes a corresponding decrease of the reaction speed. Oxalic and phosphoric acids were used in excessive amounts as complex producing reagents. The concentration of the H⁺ ions was 0.144 M. The kinetic study showed that I reacted with oxalic acid according to the equation: H₂MoO₄ + H₂C₂O₄ = [MoO₂C₂O₄]⁻

-26-

Card 1/2

"APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2

YATSIMIRSKIE, K.B.

APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2"

"APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2

APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2"

"APPROVED FOR RELEASE: 09/19/2001

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YATSIMIRSKIY, K.B.

APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2"

"APPROVED FOR RELEASE: 09/19/2001 CIA-RDP86-00513R001962310007-2

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"APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2

7/1/06

APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2"

"APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2

YATSIMIRSKIY KB.

Kinetic methods of quantitative analysis. III. Determination of small amounts of

Made with 1.9-0.1 X 10⁻³ mole of 0.1% NaSCN per ml

APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2"

Yatsimirskiy, K.B.

G-1

USSR/ Analytical Chemistry - General Questions

Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11981

Author : Yatsimirskiy K.B., Astasheva A.A.
Title : Use fo Solutions of Thiourea in Volumetric Analysis
(Thiocarbanidometry)

Orig Pub : Zh. analit. khimii, 1956, 11, No 4, 442-446

Abstract : To 10-25 ml 0.025-0.2 M solution of thiourea (I) is added an indicator (15-20 drops of saturated solution of diphenylcarbazide (II) in alcohol or 10 drops of an analogous solution of β -nitroso- α -naphthol (III)), the mixture is diluted to 100-150 ml and titrated with a solution of $Hg(NO_3)_2$. On addition of II the solution acquires, at the transition point, a blue-violet coloration, while on addition of III it changes color from yellowish-green to yellowish-orange. Mean quadratic deviation is of 0.2-0.3% with II, and 0.1-0.2% with III. Back titration is also possible, although it is more appropriate, in the determination of Hg,

Card 1/2

G-1

USSR/ Analytical Chemistry - General Questions

Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11981

to add a predetermined excess of I, and to titrate it thereafter with a solution of $Hg(NO_3)_2$. A pH value of 2 is optimal. Ag^+ , Cd^{2+} , Pb^{2+} , Zn^{2+} , Ni^{2+} , Mn^{2+} , Mg^+ , NH_4^+ ,

CH_3COO^- , SO_4^{2-} , NO_3^- and PO_4^{3-} do not interfere. I is used

also in the determination of Cd. To 20 ml of Cd-salt under study (0.01-0.05 M) are added 20 ml 0.25 M solution of I, 30-40 ml of saturated solution of picric acid, and the volume is brought up to 100 ml. After 15-20 minutes it is filtered through a dry filter and an aliquot portion (20 ml) is titrated with 0.25-0.05 M solution of $Hg(NO_3)_2$, using II as indicator. Mean quadratic deviation 0.23%. Lowest limit of determination $5 \cdot 10^{-4} M$. Determination is interfered with by Hg , Bi , Ag , Cu , Tl and large amounts of Pb . A 1000-fold excess of Zn does not decrease the accuracy, but delays substantially separation of precipitate.

"APPROVED FOR RELEASE: 09/19/2001

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APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2"

YATSIMIRSKIY, K.B

USSR/Analytical Chemistry - General Questions, G-1

Abst Journal: Referat Zhur - Khimiya, No 19, 1956, 61780

Author: Yatsimirskiy, K. B., Gruin, I. P., Kashirina, F. D.

Institution: None

Title: Determination of the pH of Alkaline Solutions by Means of Light Filters

Original Periodical: Zavod laboratoriya, 1956, 22, No 3, 271-273

Abstract: For determination of pH of alkaline solutions by means of a set of indicators and a photometer with light filters (Referat Zhur - Khimiya, 1955, 21380) the following indicators are suitable: tropeolin OOO, eosin, 2,4-nitrophenyl-azo-1-naphthol-4,8-disulfonic acid Na salt, alizarine red and tropeolin O. The pH interval is 7.5-13.4. Error of the method ~0.1. At very high values of pH the presence in the solution of ions carrying a large charge interferes.

Card 1/1

"APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2

VATCIEKIV KB

APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2"

YATSIMIRSKIY, K. B.

USSR/Physical Chemistry - Crystals, B-5

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 195

Author: Kapustinskiy, A. F., and Yatsimirskiy, K. B.

Institution: None

Title: Lattice Energy of Salts Formed by Ions with 8-Electron Outer Shells

Original Periodical: Zh. obshst. khimii, 1956, Vol 26, No 4, 941-948

Abstract: In the formula for the calculation of the energy of the crystal lattice $U = 287.2 \left[\sum n Z_K Z_A / (r_K + r_A) \right] / \left[1 - \rho / (r_K + r_A) \right]$ (Kapustinskiy, Zh. obshst. khimii, 1943, Vol 13, 497) the value of the repulsion coefficient ρ depends on the sum of the ionic radii $\rho = 0.345 - 0.00870 (r_K + r_A)^2$. Using this empirical expression the following equation can be obtained: $U = 287.2 \times \left[\sum n Z_K Z_A / (r_K + r_A) \right] / \left[1 - 0.345 / (r_K + r_A) + 0.00870 \times (r_K + r_A)^2 \right]$, which gives values of U which agree with experimental values within 2% for salts of the type MX and MX_2 . The equation also gives satisfactory results for salts of the type MX_3 . Considerable deviations are observed in the calculation of U for salts in

Card 1/2

USSR/Physical Chemistry - Crystals, B-5

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 195

Abstract: which the cations are highly polarized. The value of U has been calculated for the oxides, sulfides, and selenides of the elements in groups I and II of Mendeleev's periodic system. The values of the electron affinity of the atoms O, Se, and S have also been calculated.

Card 2/2

Yatsimirskiy, K. B.

C

Category: USSR

Abs Jour: RZh--Kh, No 3, 1957, 7802

Author : Yatsimirskiy, K. B.

Inst : Not given

Title : On the Question of Step-By-Step Complex Formation

Orig Pub: Zh. Obshch. Khimii, 1956, Vol 26, No 7, 2083-2084

Abstract: A review article. See RZhKhim, 1956, 19015.

Card : 1/1

-23-

"APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2

APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2"

YATSIMIRSKIY, K. B.
USSR/Chemical - Physical chemistry

Card 1/1 Pub. 14.7 - 4/35

Authors : Yatsimirskiy, K. B., and Vasil'yev, V. P.

Title : Determination of instability constants of complexes by colorimetric measurement of the pH of the solution

Periodical : Zhur. fiz. khim. 30/1, 28-33, Jan 1956

Abstract : A new method was developed for colorimetric determination of pH in highly dilute sodium pyrophosphate solutions. The method was tested on several series solutions containing calcium nitrate and sodium pyrophosphate and was found to be perfectly suitable for such type of measurements. The instability constant of a calcium pyrophosphate complex was computed on the basis of results obtained by this new method. Five references: 3 USSR and 2 USA (1928-1954). Tables; graph.

Institution : Chemicotechnological Institute, Ivanovo

Submitted : March 14, 1955

YATSIMIRSKIY, K.B.

Category: USSR / Physical Chemistry
Thermodynamics. Thermochemistry. Equilibrium. Physico-
chemical analysis. Phase transitions.

B-8

Abs Jour: Referat Zmtr-Khimya, No 9, 1957, 29880.

Author : Yatsimirskiy K.B., Vasil'yev V. P.

Inst : not given

Title : Thermochemistry of Pyrophosphate Complexes in Solution

Orig Pub: Zh. fiz. khimii, 1956, 30, No 4, 901-911

Abstract: Determination of the heat of mixing values of solutions of nitrates of Ni, Cu, Zn and Pb with solutions of sodium pyrophosphate of different concentration, and also of the heat of dilution of the above-stated salts. The determinations were carried out in the previously described calorimeter (RZhKhim, 1955, 32011) which has been improved by the authors. From changes in heat of mixing value, with change in concentration of sodium pyrophosphate solution, the stepwise constant of instability of $\text{Ni}(\text{P}_2\text{O}_7)^{4-}$ was calculated. Enthalpy change (ΔH) in the reaction $\text{Ni}^{2+}\text{aq} + \text{P}_2\text{O}_7^{4-}\text{aq} = \text{NiP}_2\text{O}_7^{2-}\text{aq}$ (1) is 4.21 ± 0.04 kcal.

-10-

Card : 1/2

Category: USSR / Physical Chemistry.
Thermodynamics. Thermochemistry. Equilibrium. Physico-chemical analysis. Phase transitions.

B-8

Abs Jour: Referat Zhur-Khimiya, No 9, 1957, 29880

Author : Yatsimirskiy K. B., Vasil'yev V. P.
Inst : not given

In reactions of the type $M^{+} \text{aq} + 2P_{\text{O}_7}^{4-} \text{aq} = M(P_{\text{O}_7})_2^{+} \text{aq}$ (2) the ΔH for Ni, Cu, Zn and Pb is, respectively, 2.00 ± 0.02 ; -0.67 ± 0.07 ; 2.64 ± 0.05 and -1.01 ± 0.11 . Values of standard heat of formation have been calculated for the complex ions $\text{NiP}_2\text{O}_7^{+}$ and $\text{M(P}_2\text{O}_7)_2^{+}$ ($\text{M} = \text{Ni, Cu, Zn and Pb}$). For reactions of type (2) change of isobaric thermodynamic potential and entropy have been calculated. Entropy change in these reactions satisfies the equation: $\Delta S = 0.1 L_1 + \text{const}$ (3), where L_1 is heat of hydration of M^{+} ion. Equation (3) is utilized to calculate the instability constant of Pb ($P_2\text{O}_7$)²⁻ ion, together with the thermochemical data.

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Card : 2/2

"APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2

PMM

APPROVED FOR RELEASE: 09/19/2001

CIA-RDP86-00513R001962310007-2"

DRAKIN, S. I. and YATSIMIRSKIY, K. B. (Ivanovo)

"The Entropy of Ion-Solvation,"

Report presented at Conference on the Effect of Solvents on the Properties of
Electrolytes, Khar'kov, 14-16 Oct '57.

Zhurnal Fizicheskoy, Khimii, 1958, Vol 32, Nr 4, pp 960-962.

YATSIMIRSKIY, K. B.

"Determination of phosphate, sulfate, and molybdate."

report presented at The Use of Radioactive Isotopes in Analytical
Chemistry, Conference in Moscow, 2-4 Dec 1957
Vestnik Ak Nauk SSSR, 1958, No. 2, (author Rodin, S. S.)

YATSIMIRSKIY, K.B.

Observations on B.F. Ormont's article "Present state of the theory
of complex compounds" (reports No.1 and 2). Zhur. neorg. khim. 2
no.8:1975-1977 Ag '57. (MIRA 11:3)

(Complex compounds)
(Ormont, B.F.)

AUTHORS:

Yatsimirskiy, K.B. and Tetyushkina, V.D.

566

TITLE:

Influence of Ionic Force on the Instability Constants of Halogen and Pseudo-Halogen Complex Compounds. (O Vliyanii Ionnoy Sily na Konstanty Nestoykosti Galogenidnykh i Psevdogalogenidnykh Kompleksnykh Soedineniy).

PERIODICAL:

"Zhurnal Neorganicheskoy Khimii" (Journal of Inorganic Chemistry), Vol.11, No.2, pp.320-329. (U.S.S.R.) -1957

ABSTRACT:

The range of applicability of empirical equations such as that of Davies (9) and the concepts of ionic force is still undecided. The research described is a contribution on this problem and involved the optical investigation of the thiocyanate complex of iron in the visible part of the spectrum. Relatively low concentrations of ferric nitrate (0.004974 mol/litre) and potassium thiocyanate (0.0004977 mol/litre) were used, enabling a wide range of ionic forces, from 0.25 to 3.5, to be covered. The bromide complex was also studied. Potassium, magnesium and aluminium nitrates were used to produce definite ionic forces.

Determinations were thus made of the instability constants and of the influence on complex-formation equilibria in the systems Fe^{3+} - CNS- electrolyte and Fe^{3+} - Br- electrolyte. It was shown that the ionic-force concept is valid up to forces of the order of 1.5 if the accuracy limit for the instability-constant indices of the complexes is taken as ± 0.1 ;

Card 1/2